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The proceedings consist of 97 technical papers covering such areas as analytical methods for photochemical oxidants and precursors; causes of urban, suburban, and non-urban oxidant; biological effects; oxidant control strategies; and trends in emissions and emission control technology. The International Conference was held in Raleigh, N.C. in September 1976. This volume contains the following: Physiological effects of oxidants, effects of [illegible] on vegetation, reactivity and its use in oxidant-related control, atmospheric chemistry and physics, mathematical models of ozone/oxidant air quality, oxidant-precursor relationships and their interpretation in terms of optimum strategy for oxidant control, control of oxidant precursor [illegible]

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PREFACE

Since the late 1940's when the first studies of atmospheric pollution began, photochemical smog has been evolving into a full-fledged problem with an enormously strong and complex impact upon man's lifestyle. Smog is no longer a subject of mainly academic interest. Its presence and consequences are now fully felt by the layman and perhaps most painfully by the automobile user. The use of automobiles is being restricted in the large urban centers in the U. S., and even more restrictive measures including gasoline rationing have been considered. The merits of the economic incentives traditionally associated with industrial growth are now being seriously questioned, and pressures grow stronger for a review and a more realistic appraisal of the environmental, energy, and industrial growth priorities. Such a strong and multifaceted impact of the photochemical pollution problem makes it imperative that all judgment regarding the causes, occurrence, and solution or alleviation of the problem be made responsibly and with the highest degree of confidence. Thus, while it is extremely important that the health and welfare of the people be protected, it is equally important to ascertain that such protection is really achieved and that the health danger is not traded for other equally bad or worse problems.

Intensive studies conducted in the past 3-4 years have resulted in an abundance of suggestive evidence that in part supported and in part refuted the earlier understanding, but did not resolve all existing issues. Thus, the international scientific community is still divided on the issue of the justification of the 0.08-ppm ambient air quality standard for oxidant, one objection arising from the questionable achievability of such a standard. A newly revived issue of major importance pertains to the relative roles of the hydrocarbon and nitrogen oxide precursors in the urban and rural oxidant formation processes. The viewpoint of the U.S. Environmental Protection Agency supporting maximum control of the hydrocarbon and limited control of the NO_x emissions is challenged in several Conference papers. More specific issues raised by the new evidence, and debated in the Conference, are the achievability of the ambient oxidant standard, the role of stratospheric ozone, the role of the natural ozone precursors, the utility of current air quality simulation models, and the significance of short- and long-range photochemical pollution transport.

Aside from the debate on the above issues, the Conference will gather and bring into focus the latest developments in the areas of physical-chemical research methodology, biological effects of oxidants, and emission control methods. It was felt that inclusion of such widely diverse subject areas would be essential for examining the balance, rationality, and effectiveness of the entire oxidant control effort.

The Conference is expected to be extremely valuable to the U.S. Environmental Protection Agency in that it will provide a forum for presenting the Agency's evolving viewpoint on oxidant control strategies, and for sounding out scientific receptivity to this viewpoint. The Conference is of value also to the international community of scientists and government administrators in that it will provide an opportunity for comparing the problems, experiences, and control policies of one country with those of others. Considering the now established international range of pollution transport, and the implications of oxidant-related control upon international trade, such interaction among countries is more than justified. For these reasons the organization of the Conference was undertaken by the U.S. Environmental Protection Agency, with the patronage of the Organization for Economic Cooperation and Development.

B. Dimitriades

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11-4

BIOCHEMICAL INDICES OF NITROGEN DIOXIDE INTOXICATION OF GUINEA PIGS FOLLOWING LOW LEVEL-LONG TERM EXPOSURE

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D. E. Gardner, and D. L. Coffin*

ABSTRACT

In an effort to determine possible enzymatic indicators of nitrogen dioxide (NO_2) damage and to evaluate protective mechanisms, lung and red blood cells (RBC) glutathione peroxidase (GSHP), lung and plasma lysozyme (LYZ), lung and plasma acid phosphatase (AP) and RBC acetylcholinesterase (CHE) levels were determined in guinea pigs after 7 days or 4 months exposure to 0.5 ppm NO_2. Short-term exposure depressed RBC GSHP and elevated lung LYZ and RBC CHE. Long-term exposure depressed RBC GSHP, plasma LYZ, AP and CHE but elevated lung AP. Depression of RBC GSHP and lack of induction of lung GSHP suggest this enzyme is not protective against NO_2. Damage responses dominate short-term exposures as shown by the release of creatine phosphokinase isozymes while long-term exposures may represent alterations in cell populations. Long-term effects on lung LYZ and RBC GSHP may represent differences from ozone (O_3) intoxication. Evaluation of protective agents and indicators of intoxication require chronic exposures as short-term exposures are not equivalent.

INTRODUCTION

As evidenced by this Symposium, exposure to oxidant gases continues to be a pressing human health problem. The development of tests for early damage from inhaled pollutants remains an elusive and critical aspect of this problem. Discovery of sensitive indicators of pollutant damage could result in better estimates of the health hazards of exposure and potentially indicate the underlying basic mechanism of intoxication.

Both nitrogen dioxide (NO_2) and ozone (O_3) catalyze the peroxidation of unsaturated fatty acids found in biological membranes (1). Peroxidation is highly damaging to the function of cells and is a potential common mechanism of intoxication for oxidant gases. Glutathione peroxidase (GSHP) may represent a detoxification mechanism for lipid peroxides (2), and is elevated in rats on short term (7 day) exposure to ozone, but not nitrogen dioxide (3). Creatine phosphokinase (CPK), lactate dehydrogenase (LDH), serum glutamic oxalic transaminase (SGOT), and serum glutamic pyruvic transaminase (SGPT) are released from heart, liver, and muscle on damage and may indicate damage to lung and other tissues following NO_2 inhalation. Lysozyme is likely to be released into the serum from damaged alveolar macrophages rich in this enzyme (4,5), while acid phosphatase is an enzyme found in lung lysosomal fractions capable of tissue digestion (4). Another index of potential distal injury on NO_2 inhalation is plasma cholinesterase (6).

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Since most of these indicator enzymes have been evaluated only on short-term exposures of 7 days or less to oxidant gases, the response to a near ambient level of NO_2 (0.5 ppm) was examined in both short-term (7 days) and long-term (4 months) exposure.

METHODS AND MATERIALS

Guinea pigs of the Hartley strain (250-300g, Murphy Breeding Labs) were exposed to 0.50 ± 0.04 ppm of NO_2 for 8 hours per day for 7 days or for 4 months as previously described (7). At the end of the appropriate time period the animals were exsanguinated by cardiac puncture, and the organs removed and frozen on dry ice. The organs were kept frozen until analysis. Blood was collected with 10^{-4}M EDTA to prevent coagulation, and red blood cells (RBC) and plasma were obtained by centrifugation. A comparable control group was exposed to charcoal filtered air and sacrificed in an identical manner. All of the animals were randomized from the same group of animals obtained from the supplier.

Lungs were homogenized in 9 ml of isotonic phosphate buffer for each gram of tissue. The homogenate was centrifuged at 100,000 g for 1 hour and the supernatant, soluble fraction was used for the measurement of GSH peroxidase, acid phosphatase, lysozyme, and protein (8). GSH peroxidase was determined using cumene hydroperoxide as the substrate and coupled with added GSH reductase at pH 7.6 (2). Acid phosphatase was determined by the method of Bessey et al. using *p*-nitrophenyl phosphate as a substrate in 300 mM acetate buffer at pH 5.0 (9). Lysozyme was determined in the soluble fraction and plasma by the Worthington (Freehold, New Jersey) assay kit procedure, which utilized a turbidometric determination of the digestion of *Micrococcus lysodeikticus* at pH 6.2. Results are reported as equivalent amounts of crystalline egg while lysozyme (10).

Plasma cholinesterase was determined as described before (11), using dibutyryl thiocholine as the substrate at pH 7.5. RBC GSHP levels were determined using hemolysates and the conditions described above. Plasma enzymes, lactic dehydrogenase (LDH), creatine phosphokinase (CPK), glutamic oxalic transaminase (SGOT), and glutamic pyruvate transaminase (SGPT) were determined as previously described (12). Gel electrophoresis was used to separate the isomeric forms of LDH and CPK.

Student's "t" test was used to compare the means calculated from the individual values. The numbers of animals examined in each assay are shown in the figures. Each value represented an average of three assays per animal.

RESULTS AND DISCUSSION

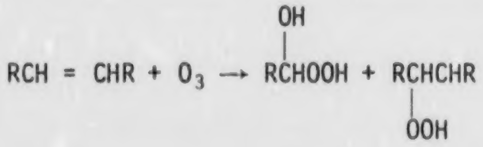
Many of the studies of the biological effects of oxidants have focused on short-term exposure on the assumption that little or no change in the response of the animal occured on continued exposure. It is now clear that exposure to oxidants results in a complex, time-dependent response on the part of the animal. The short-term effects observed in our studies are contrasted to those observed after prolonged exposure.

The exposure schedule selected for these experiments was an 8-hour exposure per day for either 7 days or for 4 months. Guinea pigs were randomized and selected from the same group that was ultimately exposed for 4 months, and the 7-day exposed animals represented a subsample of the original group of animals.

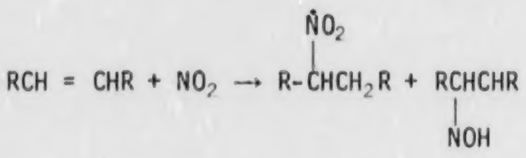
Short-term exposure is characterized by indices of tissue damage. An elevation of the serum enzymes LDH, CPK, SGOT, and SGPT was observed (Figure 1). The elevations of enzymic activity were variable with only the total CPK levels being marginally significant statistically. Because of the large variability of the enzyme levels in the NO_2-exposed group, these enzymes are of little value as specific indicators of NO_2 damage. The elevation of the CPK and LDH activity was examined in detail by gel electrophoresis. No specific tissue isoenzyme pattern could be discerned and, therefore, probably represents a non-specific type of cell damage.

Short-term exposure to NO_2 also resulted in a marked elevation of the plasma cholinesterase (Figure 2), while long-term exposure resulted in a depression of this enzyme. CHE levels are most indicative of hepatic and myocardial disease. CHE is elevated in hemochromatosis, but depression of plasma CHE is most often associated with active heptocellular disease (6,13). Increased plasma levels of CHE are seen with cardiac surgery but depressed values are consistently associated with myocardial infarction (13). Aside from secondary metastatic carcinoma of the liver, pulmonary disease, including pneumonia, is not associated with changes in CHE levels. Most likely the alterations observed, especially the depression of CHE levels on long-term exposure, are related to hepatic injury.

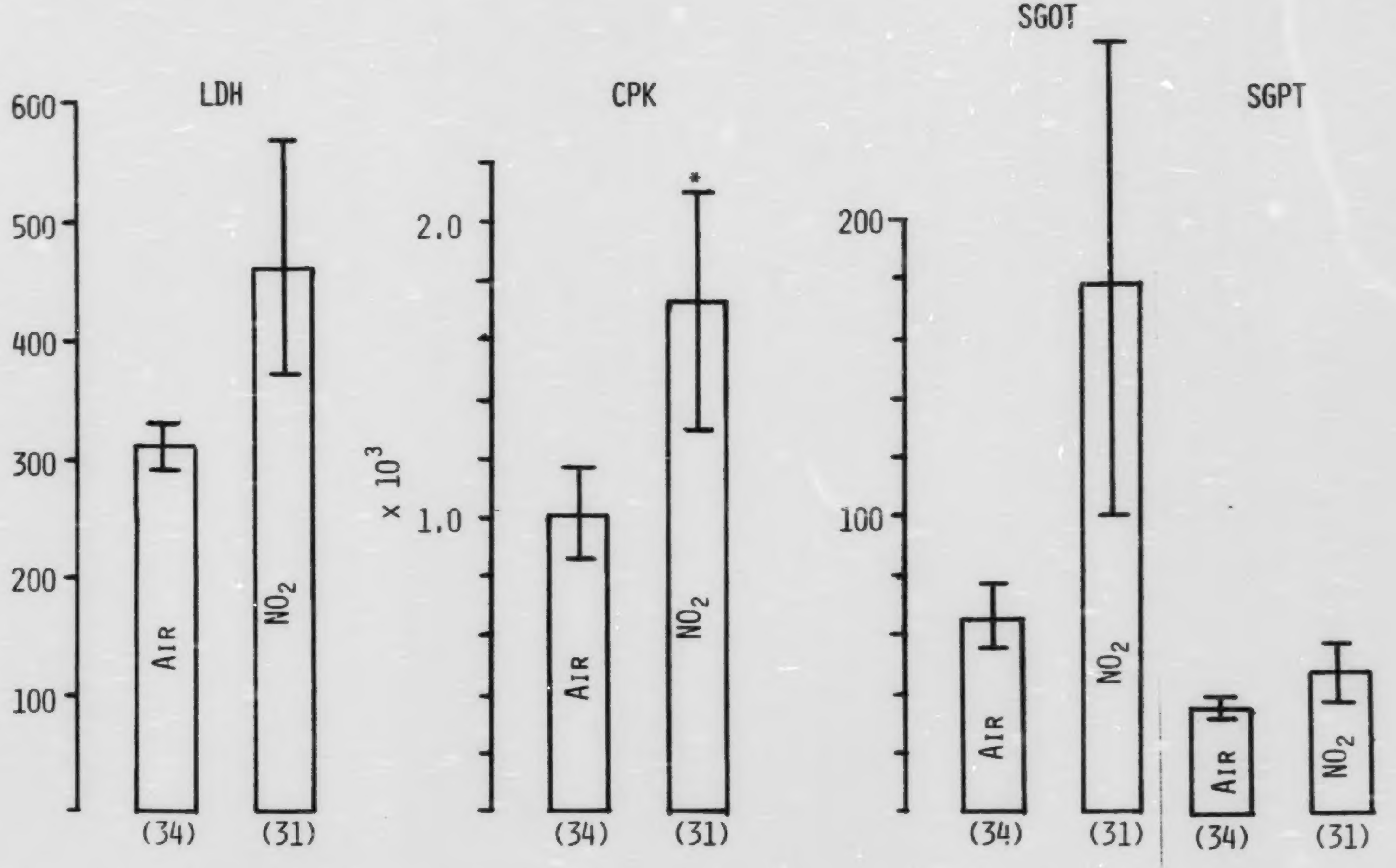
Both ozone and NO_2 catalize the peroxidation of unsaturated fatty acids:



$$RCH = CHR + O_3 \longrightarrow R\overset{\overset{OH}{|}}{C}HOOH + RCH\underset{\underset{OOH}{|}}{C}HR$$



$$RCH = CHR + NO_2 \longrightarrow R\text{-}\overset{\overset{\dot{N}O_2}{|}}{C}HCH_2R + R\underset{\underset{NOH}{|}}{C}HCHR$$



* $P > 0.05$

Figure 1. Effect of 7 day exposure on serum enzymes.

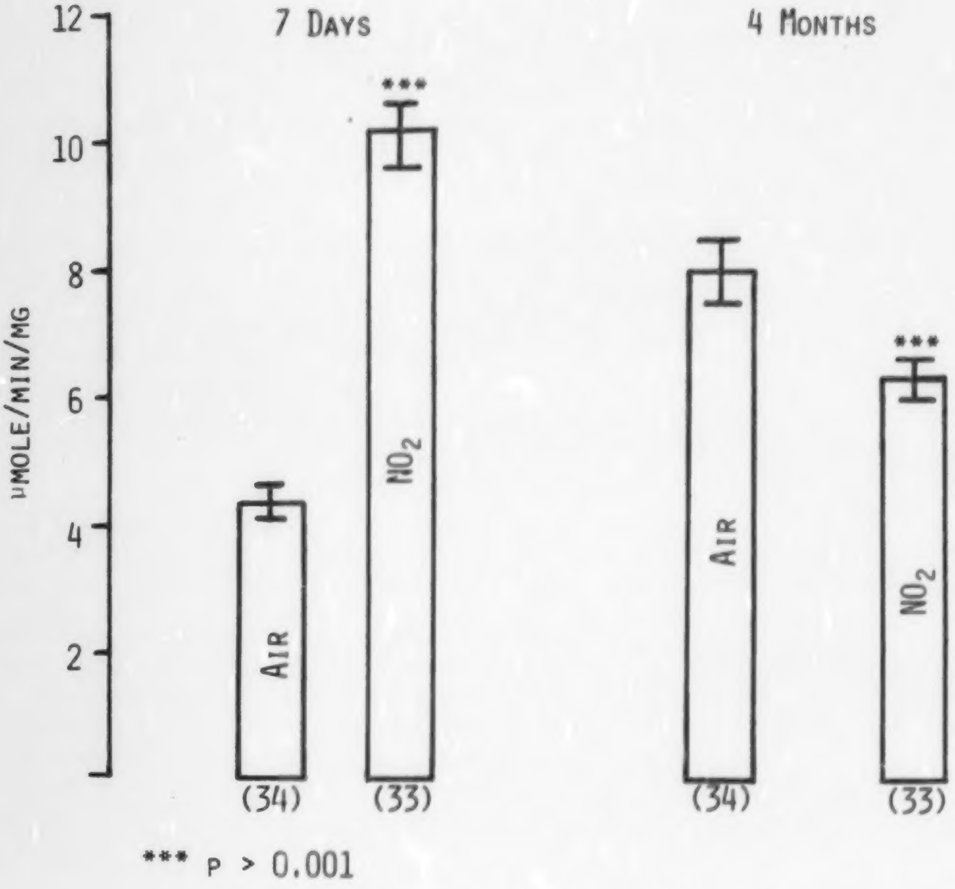


Figure 2. Effect of NO_2 exposure on plasma cholinesterase.

We have suggested that peroxidation of unsaturated lipids is a common mechanism of toxic action of both of these gases (1). Another indicator of RBC damage, Heinz body formation, has been observed with fatty acid ozonides and ozone exposure (14). Ingestion of vitamin E by both mice and men results in protection of circulating RBCs against ozonide initiated Heinz body formation (15) and the lethal effects of NO_2 and ozone in rats (16). Vitamin E as a membrane-bound antioxidant in cells may act to prevent the propagation of peroxidative damage within the cell membranes (17).

Glutathione peroxidase (GSHP) has been proposed to act as a detoxification mechanism for lipid peroxides formed during ozone inhalation (3).

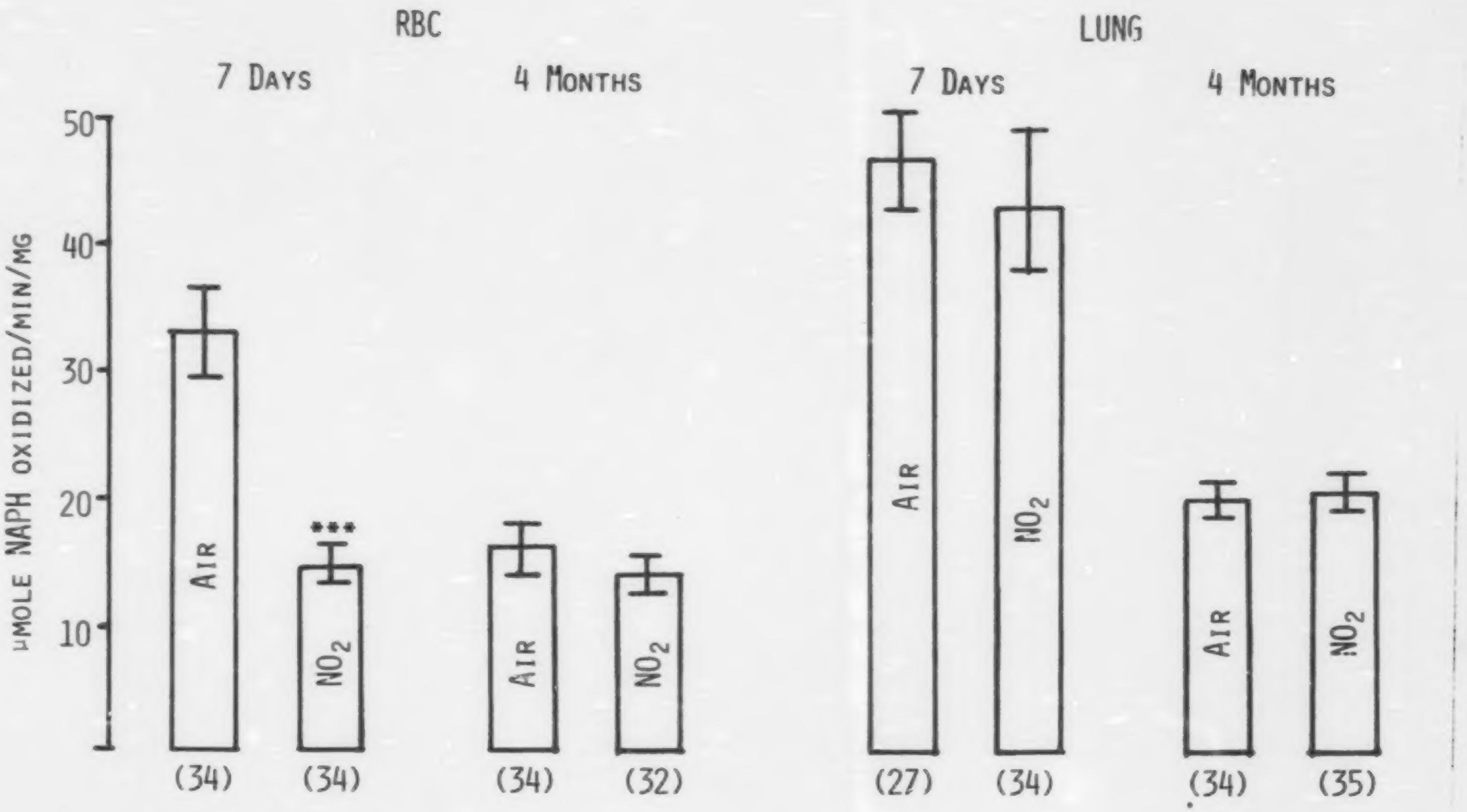
$$\mathrm{2GSH + ROOH \xrightarrow{GSHP} GSSG + ROH + H_2O}$$

$$\mathrm{GSSG + NADPH \xrightarrow[Reductase]{GSH} 2GSH + NADP^+}$$

GSHP is dependent upon glutathione reductase and NADP-reductase for full activity. In the RBC glucose serves as the source of electrons for reduction of NADP via glucose-6-phosphate dehydrogenase. Ozonide-initiated Heinz body formation is not inhibited by glucose in vitro suggesting that glucose dependent pathways of detoxification are not as important as vitamin E reserves in the prevention of Heinz bodies. A single patient with glucose-6-phosphate dehydrogenase deficiency was observed to have the same propensity to form Heinz bodies as the normal person having eaten an average U.S. dietary intake of vitamin E (D. B. Menzel, unpublished results).

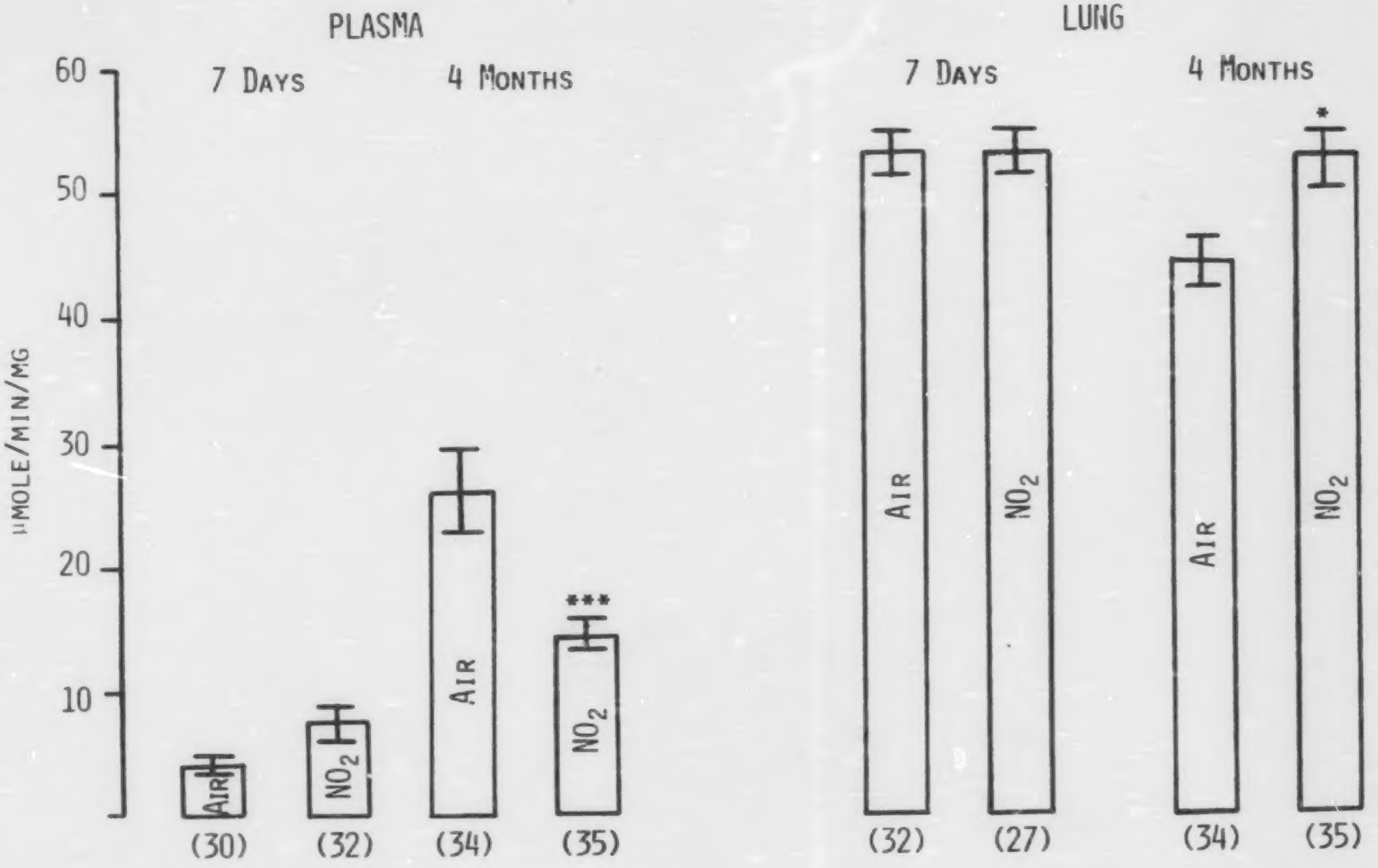
On short-term NO_2 exposure RBC GSHP levels fell, but were not depressed on long-term exposure (Figure 3). RBC and lung GSHP levels decreased with age, independent of NO_2 exposure. Chow et al.(3) have shown that GSHP levels are increased by ozone exposure of rats, but no increase in GSHP was found with NO_2. Similarly, no increases in GSHP levels were observed here. Presumably increases in GSHP on ozone exposure were to detoxify peroxides formed by ozone-initiated peroxidation. If GSHP does function as a detoxification mechanism for organic peroxides, the exposures used here to near ambient levels of NO_2 do not appear sufficient to induce higher levels of the enzyme in guinea pigs. While ozone is a more toxic gas, NO_2 produces more peroxides than ozone in model systems of polyunsaturated fatty acids (1). NO_2 exposure should induce GSHP more easily, but does not in both rats and guinea pigs. Though both ozone and NO_2 evoke strikingly similar anatomical responses and have similar chemical properties to initiate lipid peroxidation, the failure of NO_2 to induce higher levels of GSHP suggests basic differences in the mechanisms of detoxification of ozone and NO_2.

Cellular damage in the lung may result in increased phagocytosis. Lysozyme and acid phosphatase are two lysosomal marker enzymes associated with phagocytosis and repair in the lung (4). There were no immediate effects of NO_2 on the levels of the plasma acid phosphatase, but long-term exposure resulted in a significant depression (Figure 4). No effects could be detected in the lung on short-term exposure, while acid phosphatase levels were elevated on continuing exposure. The increase in lung acid phosphatase levels in the presence of depressed plasma levels suggests a continuing elevation of phagocytosis in the lung due to NO_2 exposure. Lysozyme levels were elevated in both lung and plasma on short-term exposure (Figure 5). Long-term exposure resulted in a significant depression of the levels of the enzyme in both tissues. The depression of lysozyme correlates with the increased susceptibility to airborne pathogens of NO_2-exposed animals. NO_2 exposure is likely to interfere with the defense against pathogenic bacteria.



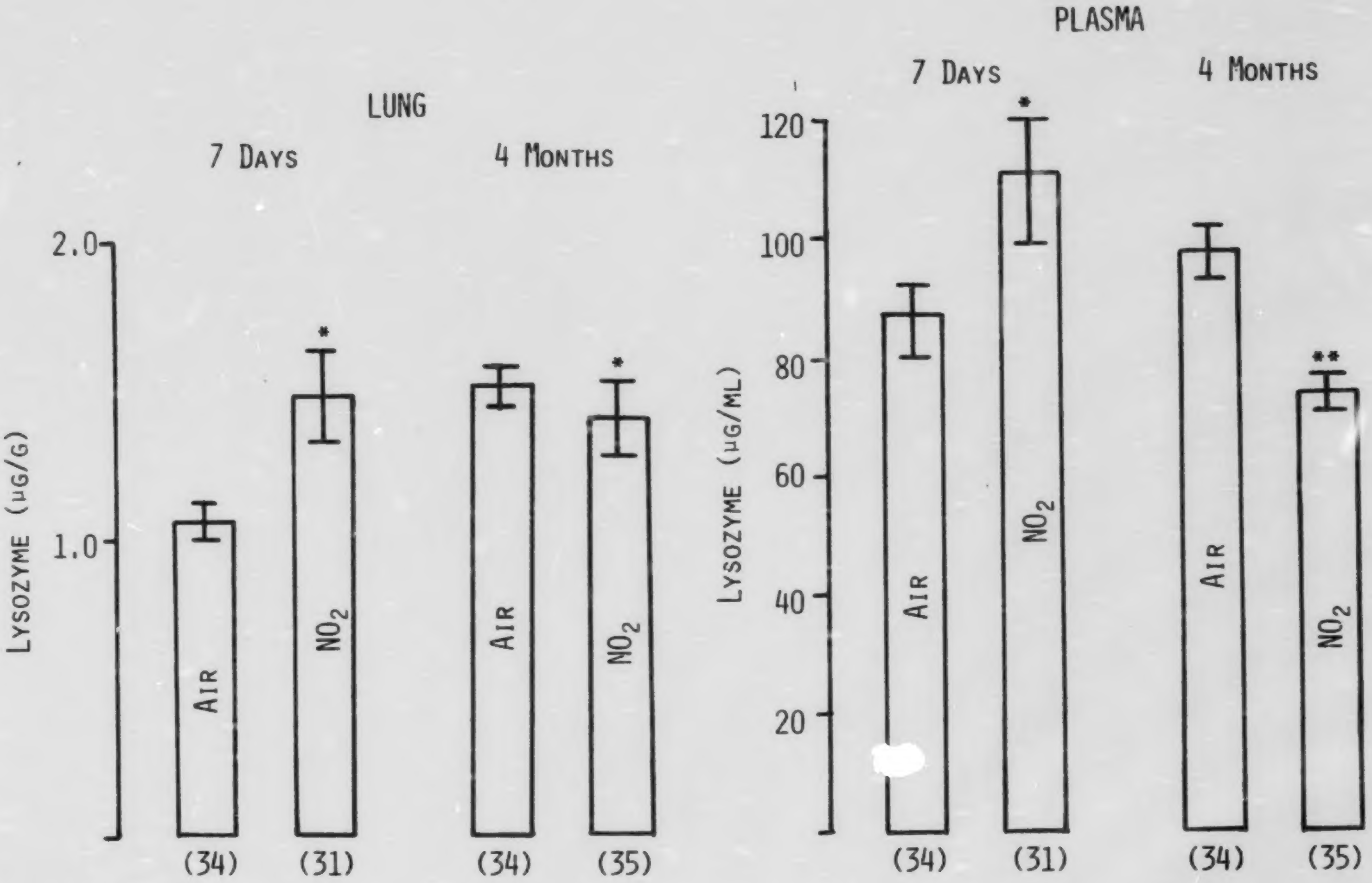
*** $p > 0.001$

Figure 3. Effect of NO_2 exposure on glutathione peroxidase levels.



* $p > 0.05$ *** $p > 0.001$

Figure 4. Effect of NO$_2$ exposure on plasma and lung acid phosphatase levels.



* $p > 0.05$ ** $p > 0.01$

Figure 5. Effect of NO_2 exposure on lysozyme levels.

In summary, of the indicators of damage studied, elevation of plasma acid phosphatase in the presence of depressed plasma lysozyme and cholinesterase appears most useful for future studies of indicators in man. Since glutathione peroxidase has not been observed to be elevated in rats or in guinea pigs on NO_2 exposure, glutathione peroxidase may not function in NO_2 intoxication as a detoxification mechanism.

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BENEFIT EFFECTIVE OXIDANT CONTROL

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ABSTRACT

A method is present for estimating oxidant health damage based on available health effect information. This method was used to analyze the spatial and temporal distribution of oxidant health damage in California. The spatial and temporal analysis shows that major portions of oxidant health damage occur during a limited number of hours that have high oxidant levels. This result suggests that significant reductions in oxidant health damage could be accomplished if oxidant levels on episode days and at the worst areas could be reduced. Although large uncertainties were found in absolute damage estimates, the relative differences in damage over space and time were found reasonably consistent when upper and lower bound estimates were made. Commonly used air quality indicators were found to be misleading predictions for damage. A change in the conceptual air pollution control model for analyzing control strategies is proposed to include direct consideration of damage.

INTRODUCTION

The mandate for air pollution control is based upon the public's desire to obtain protection against the detrimental effects of air pollution. To carry out this mandate, air quality standards have been set to identify levels of air quality desirable for protection of the public health and welfare. Air pollution control efforts are focused on the attainment and maintenance of air quality at or cleaner than the standards.

Decisions as to which strategies should be implemented for meeting or surpassing the standards are usually made considering factors such as cost, expected emissions reduction, expected improvement in air quality, and whether air quality standards would be met. Benefits of control efforts are considered in terms of improved air quality, not in terms of reduced air-pollution damage.

We believe that in strategy evaluation a major focus needs to be on benefits in terms of reduced air-pollution damage. With this belief in mind, we analyzed oxidant health damage in California using available dose-response relationships to determine whether air quality is a suitable indicator for oxidant health damage, and whether there is a need to consider the spatial and temporal distribution of damage in air pollution decision-making.

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This paper presents a summary of our analysis. First, the method for estimating oxidant health effects is presented. This is followed by an analysis of the spatial and temporal differences in damage and then by a comparison of air-quality and health-damage estimates. Then a new conceptual model for analyzing air pollution is proposed, and benefit-effectiveness analysis is discussed.

METHOD OF ESTIMATING OXIDANT HEALTH DAMAGE

DOSE-RESPONSE RELATIONSHIPS

We based our estimates of health damage on dose-response relationships developed by Leung, Goldstein, and Dalkey (1). We considered these relationships the best available for characterizing the human health effects of oxidant in view of the paucity of available information.

Leung, Goldstein, and Dalkey conducted a delphi survey of 14 medical professionals familiar with air pollution health effects. Each professional was asked to estimate the oxidant level at which 0, 10, 50, and 90% of 14 different population subgroups would experience three levels of health impairment: discomfort, disability, and incapacity. The 14 population subgroups considered were: normal, children, old age, heart condition (mild), heart condition (severe), hay fever (sinusitis), influenza, upper respiratory infection, asthma, acute viral bronchitis, actue bacterial pneumonia, chronic respiratory disease, mild chronic obstructive lung disease, and severe chronic lung disease. A logistic equation was then used to process the information on oxidant concentrations to assess impairments for each population category:

$$\ln \frac{F}{1 - F} = A + B \ln(Ox)$$

where F = percentage of population affected

Ox = oxidant concentration to which the population is exposed for 1 hour (in ppm)

A = calculated intercept parameter

B = calculated slope parameter

This equation may be stated in the equivalent form

$$F = \frac{e^A \, Ox^B}{1 + e^A \, Ox^B}$$

What resulted was 42 dose-response functions giving percentage of population affected by hourly oxidant concentrations with three kinds of estimates: low, best, and high. The low and high estimates were at the 5 and 95% confidence levels.

COMPOSITE DAMAGE FUNCTIONS

We took the functions developed by Leung, Goldstein, and Dalkey and produced three per-capita composite damage functions by combining the 42 dose-response functions for the best, low, and high health-damage estimates. To develop each function, we weighted each subpopulation curve by our estimate of the relative size of each subpopulation group in California. In addition, we weighted the three levels of health impairment as discomfort = 1, disability = 6.6, and incapacity = 54.5. These weighting factors were based on estimated medical treatment costs and productivity loss for typical symptoms for each severity level.

POPULATION-WEIGHTED DAMAGE ESTIMATES

Next, we took the hourly oxidant air-quality data at 76 oxidant air-monitoring locations in California for calendar year 1974 and combined this with the per-capita composite health-damage functions shown in Figure 1 to obtain per-capita oxidant health damage. We then combined population data with the per-capita estimates to obtain population-weighted damage estimates. The overall method for estimating health damage resulting from oxidants is discussed in detail by Schink and Dole (2).

EVALUATION OF HEALTH DAMAGE ESTIMATES OVER SPACE AND TIME

Using the method delineated in the previous subsection, we estimated population-weighted oxidant health damages for the eight California air basins for which ambient oxidant data were available. These estimates (low, best, and high) are listed in columns 1-3 of Table 1. The results illustrate the uncertainty surrounding absolute health-damage estimates. The low (5%) and high (95%) limits are from 10% to 2600%, respectively, of the best estimate. Columns 4-6 of Table 1 show the estimated percentage share of damage for each air basin using the high, low, and best estimates.

Although the absolute damage estimates show wide variability, the percentage shares, or relative health damage estimates, for the various air basins are reasonably consistent and similar, with from 88 to 96% of the damage estimated occurring in the South Coast Air Basin. These results indicate that by far the greatest amount of oxidant health damage in California is in the South Coast Air Basin, suggesting that a major portion of the resources devoted to oxidant control in California is appropriately devoted to improving the air quality in this basin.

We believe the similarity and consistency of the relative damage estimates are largely a function of the shape of the per-capita composite damage function, not its scaling factor. Thus we expect relative damage estimates developed from different damage functions to yield similar results if the functions exhibit similar shape characteristics. We consider the important shape characteristics to be:

- Zero or minimal damage at low oxidant concentrations corresponding to

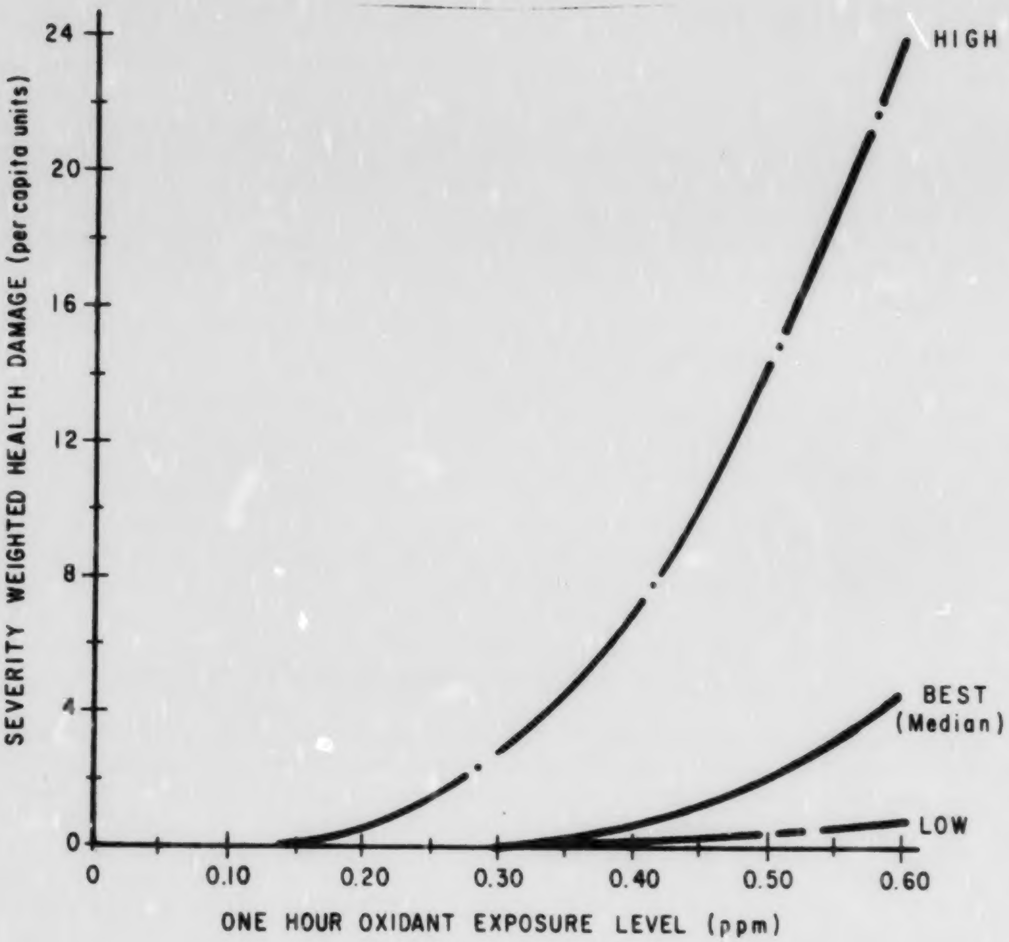

Figure 1. Composite, severity-weighted, per-capita, oxidant health-damage functions.

low or negligible risk to people at oxidant levels at or below the air quality standard.

- Increasing health damage as oxidant levels increase.
- Increasing rate of change in health damage as oxidant levels increase.

These characteristics result in the greatest amount of damage occurring at the highest oxidant levels. This result can be seen in Table 2, which shows the percent of per-capita oxidant health damage at or above various air-quality levels at Azusa, California, one of the more heavily impacted areas in the South Coast Air Basin. As indicated in the table, from 11 to 22% of the damage is estimated to result from 14 hours having oxidant levels 0.30 ppm and above during the year. From 61 to 79% of the health damage is estimated to occur during 223 hours (2.5% of the year) having levels 0.20 ppm and above.

TABLE 1. CALIFORNIA OXIDANT HEALTH DAMAGE FOR CALENDAR YEAR 1974 IN WEIGHTED HEALTH DAMAGE UNITS AND PERCENT OF TOTAL DAMAGE

Air Basin	Total damage ($\times 10^3$) Low	Best	High	% Share of total Low	Best	High
South Coast	5,955.3	57,330	1,469,263	96.30	95.22	88.50
San Diego	52.3	892	39,947	0.84	1.48	2.41
San Francisco Bay Area	62.3	688	49,696	1.01	1.14	2.99
San Joaquin Valley	59.8	683	53,672	0.97	1.13	3.23
Southeast Desert	30.2	332	22,199	0.49	0.55	1.34
Sacramento Valley	21.9	254	21,581	0.35	0.42	1.30
North Central Coast	1.2	16	2,204	0.02	0.03	0.13
South Central Coast	0.9	12	1,579	0.01	0.02	0.09
Total	6,183.9	60,207	1,660,141	99.99	99.99	99.99

This table indicates that major portions of the oxidant health damage occur during a limited number of hours that have high oxidant levels during the year, suggesting that significant reductions in oxidant health damage could be accomplished if oxidant levels on episode days could be reduced.

COMPARISON OF AIR QUALITY AHD HEALTH DAMAGE ESTIMATES

We compared health-damage estimates and commonly used oxidant air-quality parameters, highest hourly reading for the year, annual average, annual average of the daily maximum hour, and annual hours above the 0.08 ppm standard, to determine how well air quality parameters represent health damage. Per-capita health-damage and air-quality parameters for 1974 for two locations, San Jose and Upland, are presented in rows 1 and 2 of Table 3.

San Jose and Upland are the two most severely impacted locations in the San Francisco Bay Area Air Basin and South Coast Air Basin respectively. The estimated relative damage at San Jose as compared to Upland is 1.1% as shown

TABLE 2. PERCENT OF PER CAPITA OXIDANT HEALTH DAMAGE OCCURRING AT OR ABOVE SELECTED OXIDANT LEVELS AT AZUSA IN 1974

Oxidant level	Hours at or above level	Percent of oxidant damage at or above level		
		Low	Best	High
0.10	987	99	99	96
0.15	505	94	93	84
0.20	223	79	78	61
0.25	71	51	49	32
0.30	14	22	20	11
0.35	3	8	7	3

TABLE 3. PER-CAPITA OXIDANT HEALTH DAMAGE AND SELECTED OXIDANT INDICATOR VALUES FOR UPLAND AND SAN JOSE IN 1974

Location	Annual per capita health damage	1974 maximum hour (ppm)	Annual average (ppm)	Annual average of daily maximum hour (ppm)	Annual hours above 0.08 ppm
San Jose	0.68	0.22	0.020	0.052	162
Upland	60.43	0.44	0.050	0.144	1360
San Jose as % of Upland	1.1%	50.0%	40.0%	36.1%	11.9%

in row 3 of the table. A comparison of this percentage with those for the air quality parameters indicates the air quality parameters fail to capture the large difference that exists in health damage between the two locations. Thus air quality seems to be a misleading indicator of health damage.

Similarly, changes in health damage are much greater than changes in air quality. This can be seen more clearly in Table 4. This table has estimates

TABLE 4. ESTIMATED PERCENTAGE CHANGE IN OXIDANT HEALTH DAMAGE FOR CHANGES IN OXIDANT AIR QUALITY

Change in oxidant air quality	Estimated change in oxidant health damage		
	low (%)	best (%)	high (%)
20% improvement	-68	-67	-56
10% improvement	-42	-41	-32
10% deterioration	+63	+60	+42
20% deterioration	+158	+146	+95

of expected changes in health damage associated with a 10 and 20% reduction or a 10 and 20% increase in all hourly oxidant readings during the year. High and low estimates are included as well as the best estimate. The table indicates a 10% improvement in oxidant air quality is expected to yield a 32 to 42% reduction in oxidant health damage. This indicates the reduced damage expected with small improvements in air quality is much greater than one would expect when just looking at the change in air quality.

CONCEPTUAL AIR POLLUTION CONTROL MODEL

PAST MODEL AND PROPOSED MODEL

Based on the preceding comparison of health damage and air quality, we propose a change in the standard conceptual air-pollution control model illustrated in Figure 2. As shown in Figure 2, air quality, the result of the interaction of emissions, meteorology, and atmospheric chemistry, is improved through emission control. Currently, we analyze various possible emission-control strategies by means of feedback loop A, i.e., by comparing the resultant changes in air quality produced by control strategies. The goal is to improve air quality to meet air quality standards. Although air quality varies over both space and time, a single air-quality parameter (e.g., the maximum pollutant concentration as measured at the worst location in an air basin) is usually used in the analysis by means of feedback loop A.

We propose a change in the feedback loop to consider damage (loop B). Due to the large uncertainties in the absolute damage estimates, we recommend damage analysis be made on a relative basis by looking at relative differences in damage estimates associated with various strategies until more accurate absolute damage estimates can be made. Furthermore, as techniques for analyzing other aspects of damage (e.g. vegetation damage) are developed, their results can be included in the analysis.

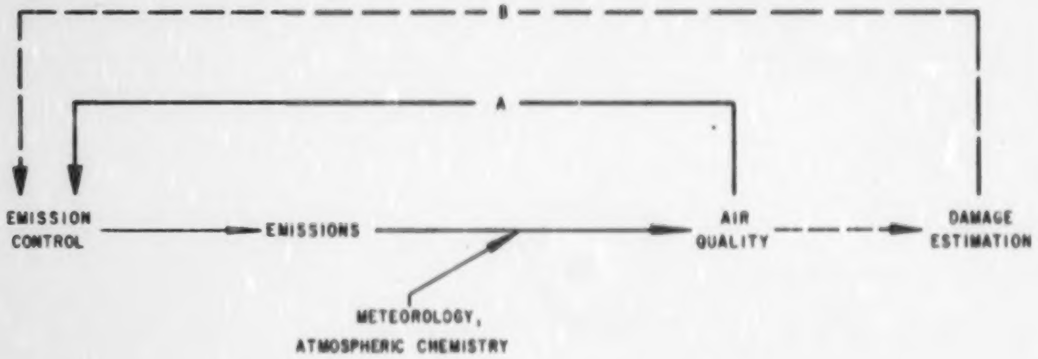

Figure 2. Conceptual air-pollution control model.

Consideration of damage represents an improvement in two ways. The first is that damage estimates place the focus more clearly on the parameter of greatest concern to the public. As was noted earlier in this paper, commonly used air quality parameters appear to be misleading indicators of oxidant health damage. The second improvement involves consideration of the spatial and temporal variations in damage. This consideration is accomplished by using damage functions (dose-response relationships) and receptor population weighting factors to provide a weighting scheme for totaling damage over space and time.

BENEFIT-EFFECTIVENESS EVALUATION

With the consideration of damage by means of loop B, benefit-effectiveness evaluations can be made. Benefit-effectiveness evaluation involves the analysis of benefits (reduced damage) associated with various options or strategies to determine how to maximize the benefits for a given allocation of resources. These evaluations would consider the spatial and temporal distribution of damage and would identify control options providing the greatest reduction in damage for a given abatement cost. Though beyond the scope of this paper, we believe alternative control strategies can be evaluated within a stochastic nonlinear mathematical programming framework using weighted damage as an objective function. This function would be minimized subject to input and/or expenditure level abatement cost constraints.

CONCLUSIONS

1. Relative health damage estimates are reasonably consistent over space and time, even though there are wide variations in absolute estimates.

2. Air quality appears to be a misleading indicator of health damage. Commonly used air-quality parameters do not capture the large variation in the spatial and temporal differences in health damage.

3. Significant reductions in per-capita oxidant health damage can be achieved

if reductions are made at the worst locations at the time of the worst oxidant damage. Thus, oxidant health damage could be significantly reduced if oxidant levels on episode days could be reduced.

4. Air pollution decision-making on which strategies to use needs to consider benefits in terms of reduced damage. This consideration may be accomplished by using relative damage estimates in benefit-effectiveness evaluation.

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SESSION 12

EFFECTS OF OXIDANTS ON VEGETATION - I

Chairman: W.W. Heck
North Carolina State University at Raleigh

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OZONE INDUCED ALTERATIONS IN PLANT GROWTH AND METABOLISM

D. T. Tingey*

ABSTRACT

Plant foliage is a primary receptor of ozone and other oxidants that cause biochemical and physiological changes in the foliage and these foliar changes are reflected in the development of other plant organs. The biochemical changes that are induced by ozone are the cause of visual injury, growth reduction, loss of plant vigor, and ultimately determine plant community and broader ecosystem levels of response. Changes in plant physiology and biochemistry can provide sensitivity markers and indicators of pollutant injury, growth, yield, and quality effects.

One of the earliest indicators of ozone effects on plants is the production of stress ethylene. This ethylene is produced by the plant in response to ozone, and a close relationship exists between the amount of injury and the amount of stress ethylene produced. In addition, ethylene can increase leaf abscission and phenol biosynthesis and induce biosynthesis of enzymes involved in lesion formation.

When plants are exposed to chronic levels of ozone, less sugar is stored in the roots. Chronic exposures also cause an increase in the phenol content of the foliage, which occurs prior to the appearance of visual injury. The phenol increase is also related to the ultimate foliar injury and the stipple symptom seen in injured tissue is frequently the result of phenol accumulation.

The effects of ozone are not limited to the foliage. In general, the effects of the ozone occur first on root growth followed by top growth. When the production of photosynthate is limited, plants restrict the flow of carbohydrates to the roots.

Chronic effects of ozone are not limited to symptomology and reduced growth, as ozone can also alter quality (e.g., by increasing the nitrogen (N) content of the foliage). Even though there is higher N in the leaves of forage plants, they provide less protein/unit area of crop cover. This has the net effect of reducing the forage protein available to animals. Forage crops also exhibit a decrease in β-carotene content.

These physiological changes help explain why alterations in growth and plant vigor can occur. The retention of carbohydrate in the leaves reduces the growth of the roots and results in less energy stored. This reduction in

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stored energy will ultimately slow plant growth and render the plant more sensitive to other stresses. Physiological changes provide a sensitive means of monitoring the health and vigor of the plant with or without visual injury.

INTRODUCTION

Plants exist in two different environments: the foliage and stems are immersed in a gaseous environment while the roots in the soil have only limited gas exchange. Even though the plant survives in two different environments, plant growth is the summation of the interaction of events that occur in the shoot and root. As a whole, the plant is autotropic while the individual organs are heterotrophic depending upon one another for specific assimilated or elaborated substances (1). The roots supply water, minerals, nitrogen compounds, and phytohormones. The foliage supplies carbohydrates, vitamins, cofactors, nitrogen compounds and phytohormones (1). These elaborated substances from the root and shoot are translocated throughout the plant and are required for normal growth.

Plant growth and yield is the end product of the biochemical processes related to uptake, assimilation, biosynthesis, and translocation. Growth requires that the plant photosynthetically trap solar energy and extract the necessary minerals and water from the soil. The various plant organs convert these raw materials into the required compounds for plant growth. These materials are frequently produced in excess at the site of production and are translocated throughout the plant. If the distribution of assimilated or elaborated substances among the plant's organs is disrupted, a reduction in growth and/or yield will result.

The foliage is the primary route by which ozone enters the plant and is also the primary site where it exerts its effect. To penetrate to the site of action, ozone diffuses across the leaf boundary layer, through the stomatal pores, which in part control the amount of ozone entering the leaf; passes through the intercellular spaces; and dissolves in the hydrated cell surfaces. When the ozone dissolves in the water, it decomposes into free radicals, which exert the ozone effect (2).

The effects of ozone on the plant can be divided into several levels, depending on the time period after exposure that the effects are observed. The earliest effects are an increase in membrane permeability, an increase in the leakage of ions such as potassium from the cell, a decrease in carbon dioxide fixation, and a stimulation of stress ethylene production (2,3). These early changes are followed by both enzyme inactivation and/or activation of other specific enzymes, alteration in metabolite pools, and modified translocation (4,5). These biochemical changes are ultimately expressed in increased leaf drop, visual foliar injury, and a reduction in plant growth and yield (6,7,8, 9). Thus plant changes that are initially biochemical in origin are ultimately expressed as visual injury, losses in plant growth and yield, and reduced plant vigor; they ultimately determine plant community and broader ecosystem levels of response.

Photochemical oxidants can depress plant growth and yield by one or a combination of several possible mechanisms, such as, reducing the carbon dioxide uptake, decreasing the amount of photosynthate formed, reducing mineral uptake from the soil, altering the amount of types of compounds elaborated by the different organs, altering the rate of translocation, or changing the source-sink relations for biosynthesized compounds among the various plant organs, or reducing the life of photosynthetic organs.

RESULTS AND DISCUSSION

Plants produce low levels of hormonal ethylene under normal conditions, but when subjected to environmental stresses, ethylene production increases. This increased ethylene production following stress is frequently referred to as wound or stress-induced ethylene. Injured, but not dead tissue is the site of the stress-induced ethylene production (10). Craker (11) suggested that the production of stress ethylene is the cause of many of the plant responses to ozone. Stress ethylene is liberated from plants by as little as 15-minutes exposure to ozone and is increased by both the amount and duration of ozone (3). The stress-induced ethylene is liberated by the plant prior to any apparent visual changes and frequently in the absence of visual foliar injury (3). Also, a close relation exists between the stress-induced ethylene and the ultimate foliar injury, indicating that stress-ethylene evolution is a good measure of ozone stress to plants (3). The maximum rate of ozone-induced ethylene production occurred within 2 to 4 hours following the exposure, and the amount of stress ethylene produced was in a physiologically active concentration (11).

Increased leaf abscission is frequently associated with oxidant injury and can result from increased stress ethylene production (6,12, Tingey unpublished data). The increased leaf abscission could result in reduced plant growth by decreasing the available leaf area for photosynthesis. Also, reduced plant growth and dwarfness in plants is associated with elevated ethylene levels (10,13). The activity of several enzymes involved with phenol biosynthesis and phenol oxidation can be increased by elevated ethylene levels (10).

Howell and Kremer (14) identified pigments formed in ozone-exposed leaves exhibiting visual injury as polymerized phenols, proteins, and amino acids. These researchers suggest that the ozone induces changes that either allow more oxygen to enter the cells or allow oxidative enzymes to react with phenols, forming quinones that can polymerize with proteins and amino acids to form the pigments seen in injured tissue. In ponderosa pine foliage, phenols increase prior to the appearance of visual injury (5). In alfalfa plants experiencing chronic ozone exposure, there is an 8% increase in total phenols (see Table 1). There is also a positive correlation between the amount of phenols that accumulate in the tissue and the amount of foliar injury (15). The activities of the enzymes of phenol biosynthesis (phenylalanine ammonia lyase) and phenol oxidation (polyphenol oxidase, and peroxidase) associated with lesion formation are stimulated prior to the appearance of visual injury (4). The increases in enzyme activities can all be stimulated by ozone-induced stress ethylene, and ethylene is apparently the trigger for lesion formation (4,10, 11). Visual injury is associated with reduced growth. Studies with radishes have shown a linear relationship between the foliar injury observed at the

TABLE 1. THE INFLUENCE OF CHRONIC OZONE EXPOSURES ON THE TOTAL GROWTH AND SOLUBLE RESERVES OF ALFALFA*

Ozone Concentration	Total Dry Matter (g)	Total Nonstructural Carbohydrates (g)	% TNC / Total Dry Matter
0	49.6	9.3	19
50	27.1	4.2	15

*For experimental details, see Reference 18.

final harvest and the percent growth reduction measured (Y = 1.6 + 0.9X, where Y = % growth reduction and X = % foliar injury to the plant; for experimental details see reference 16).

The incorporation of carbon dioxide is required for plant growth. A reduction in photosynthesis is ultimately expressed as decreased dry matter production. When plants are exposed to either acute or chronic ozone doses, there is a temporary reduction in photosynthesis. Alfalfa was exposed to a low concentration of ozone (50 nl/l, 6 hrs/day, for 10 wks) the total dry matter produced for the season was reduced 45% (Table 1). In addition, the total nonstructural carbohydrates (TNC) were reduced 55%. The exposed plants also contained lower levels of TNC as a percentage of the total dry matter than did the control plants. TNC reserves are used by the plant to drive its metabolic and growth processes in both shoots and roots.

In addition to a reduction in photosynthesis and the TNC reserves in the plant, there is also a change in the partitioning of photosynthate in plants exposed to ozone stress. In ponderosa pine exposed to ozone (100 nl/l,6 hrs/day, for 20 wks) there was a retention of sugars and starch in the top of the plant and a decrease in these metabolites in the roots (5). The reduction of soluble reserves could decrease the ability of the plants to initiate growth the following spring.

When shoot-synthesized carbohydrates bacame too deficient to maintain the normal growth rate, sinks such as roots and fruits are more severely affected than the foliage. This is consistent with the observation that organs remote from the site of synthesis or absorption are the most severely penalized under stress conditions that affect the process (1). Hence, when either storage roots, fruits, or seeds have a high demand for photosynthate, they will experience a reduction in translocated photosynthate, and growth will be reduced if an ozone stress has reduced photosynthesis during this period. This reduction in photosynthate available to the sinks during a period of high metabolic demand explains why yieled reductions are greater during specific phenological stages (16).

The root and shoot are in constant competition for energy and resources for their growth and development (1). The shoot-root ratio measures the resultant pattern of the differential growth of the two organs. The shoot-root ratio can be used to measure the effect of environmental stresses on plant growth patterns. The effect of chronic ozone exposures on the shoot-root ratios is shown in Table 2. Each species exhibited its own characteristic ratio. However, all species showed an increased shoot-root ratio even at the 50 nl/l ozone treatment. This increase could result from a stimulation of foliage growth or a reduction in root growth. But the levels of ozone used suppressed both foliage and root growth (7,8,9). Hence, the increase in the shoot-root ratio could only result from a greater suppression of root growth in relation to foliage growth. The greater reduction in root growth would be predicted from the reduction of photosynthesis, translocation, and accumulation of photosynthate in the roots reported in the above paragraphs. The reduction in root growth and stored reserves has been reported in the field (19). Studies have shown that trees experiencing air pollution stresses are more susceptible to other environmental stress (20,21).

TABLE 2. THE INFLUENCE OF CHRONIC OZONE EXPOSURES ON THE SHOOT-ROOT RATIO*

Ozone Concentration nl/l	Plant Species			
	Alfalfa	Soybean	Radish	Tobacco
0	1.1	8.9	2.2	7.3
50	1.3	9.3	4.0	11.1
100	1.7	10.0		

*For experimental details, see References 7,8 and 9.

The reduction in root growth is also reflected in reduced mineral uptake (Table 3). The uptake of phosphorus (P) and potassium (K) was reduced about 30%, while the uptake of calcium (Ca) and magnesium (Mg) was reduced approximately 45%. The reduction would be expected to result from the lowered metabolic reserves in the roots from the ozone stress. Mineral uptake is dependent on photosynthesis and metabolic reserves (22).

TABLE 3. MINERAL UPTAKE OF ALFALFA EXPOSED TO CHRONIC OZONE LEVELS*

Ozone Concentration (nl/l)	Total Plant Material, Dry (g)	Elemental Composition (mg/Total Plant Material)			
		P	K	Ca	Mg
0	1.82	11	67	20	7
50	1.51	10	61	15	6
100	0.99	8	46	11	4

*For experimental details, see Reference 9: Elemental Analyses conducted by Soil Science Department, North Carolina State University, Raleigh, N.C.

Symbiotic nitrogen fixation by legumes is controlled in part by photosynthesis and photosynthate distribution (23). The photosynthate is required in the roots to provide the energy to reduce and incorporate atmospheric nitrogen into organic forms. Nitrogen fixation was measured in alfalfa plants exposed to either 0 or 50 nl/l ozone (Table 4). The total nitrogen fixed by the plants throughout the growth period was depressed 40%. However, the efficiency of nitrogen fixation was not affected by the ozone treatment. This illustrates the dependency of nitrogen fixation on photosynthesis and growth.

TABLE 4. EFFECT OF OZONE ON NITROGEN FIXATION BY ALFALFA*

Ozone Concentration (nl/l)	Total Plant Material (TPM) (g)	Nitrogen Fixed (mg/TPM)	Efficiency (mg N/g Plant Material)
0	49.6	1350	27
50	27.1	793	29

* For experimental details, see Reference 18.

Forage quality is also altered by chronic ozone exposure (Table 5). The ozone treatment increased the content of protein, amino acid, and phenols, and decreased the level of β-carotene in the foliage.

TABLE 5. EFFECTS OF CHRONIC OZONE EXPOSURES ON THE QUALITY OF ALFALFA FORAGE*

Chemical Constituent	% of Control Level
Protein	128
Amino Acids	119
Total Nonstructural Carbohydrates	98
Phenols	108
β-Carotene	76

* For experimental details, see reference 18.

The protein increase is not of significance because total dry matter production was reduced and therefore protein production/unit ground area was also reduced (18). As a result, the amount of protein available for feed is decreased. Even though there are significant changes in the organic content of alfalfa foliage, there do not seem to be any significant changes in the mineral composition (Table 6).

TABLE 6. THE EFFECT OF CHRONIC OZONE EXPOSURES ON THE MINERAL CONTENT OF ALFALFA FOLIAGE*

Ozone Concentration (nl/l)	Elemental Composition (%)			
	P	K	Ca	Mg
0	0.6	5.0	1.4	0.5
50	0.6	5.0	1.3	0.4
100	0.7	5.1	1.3	0.4

* For experimental details, see Reference 9.

SUMMARY

Ozone concentrations near and below the current standards have been shown to have significant effects on plant growth and metabolism. The majority of effects observed, such as reduced root growth, mineral uptake, and nitrogen fixation, seem to result from reduced photosynthesis and photosynthate distribution. This reduction in metabolic reserves ultimately slows plant growth and renders the plant more sensitive to other stresses. Physiological changes can provide a sensitive means of monitoring the health and vigor of the plant with or without visual injury.

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OXIDANT LEVELS IN REMOTE MOUNTAINOUS AREAS OF SOUTHWESTERN VIRGINIA AND THEIR EFFECTS ON NATIVE WHITE PINE (PINUS STROBUS L.)

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ABSTRACT

Oxidant levels were monitored for 15 months in southwestern Virginia. Symptom development in response to oxidant levels was recorded on white pine field trees using two methods: (a) individual fasicle response, and (b) total tree response. Pollution episodes were noted in July 1975 and June 1976 and both resulted from winds out of the NE. Symptom development was reported in association with these episodes. The 1975 symptom expression appeared to be in direct response to high levels of oxidant during late June and early July. The 1976 symptom expression has indicated thus far an accumulative oxidant exposure response. Age of needle tissue and time and duration of exposure are considered to be involved.

INTRODUCTION

Since the early 1900's a disease of eastern white pine (Pinus strobus L.) generally called "needle blight" characterized by stunting, chlorosis, and/or tip necrosis of needles, has been reported throughout the range of the species. More recently, needle blight of eastern white pine has been shown to be the result of acute and chronic ozone injury (4,10). Costonis and Sinclair (10) found that ozone at concentrations of 3 pphm for 48 hours and 7 pphm for 4 hours would cause acute injury to current-season needles on white pine field trees. Large white pines have been observed in various stages of decline in the mountains and valleys in southwestern Virginia. A decline of white pine trees has been observed along the Blue Ridge Parkway with trees showing typical oxidant damage (Skelly, unpublished data, 1976).

In the Shenandoah Valley of Virginia in 1973, Morris (15) reported that 30% of the white pines in an area of Rockingham County, Virginia exhibited visible injury, and 5% were severely affected or completely brown as observed from an aerial survey. In 1971, 15 trees were tagged, and after 2 years of exposure 13 trees were shown to have declined. Of the 13 trees, six died after what appeared to be a result of three consecutive exposures. He

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estimated a 3% mortality of eastern white pine (Pinus strobus L.) in the affected area.

Recently, high levels of ozone in excess of the National Ambient Air Quality Standard (NAAQS) for photochemical oxidants have been reported; 160 microgram/m^3 or 8 pphm maximum concentration oxidant not to be exceeded more than one hour once per year.

Johnston et al. (2) monitoring ozone in rural Garrett County, Maryland, from August 29 to September 1972, found the NAAQS to be exceeded 11.26% of the time; one period lasted 26 consecutive hours. The mean for the period was 5.7 pphm. Richter et al. (1) found similar high ozone concentrations in the rural Mount Storm area of West Virginia. Coffey and Stasiuk (9) reported ozone concentrations in excess of the NAAQS common in the rural areas of New York State and suggested transport of ozone and natural ozone precursors from the stratosphere. Miller et al. (13) attributed high rural oxidant levels to the transport of oxidant and man-made precursors from the population centers in the San Joaquin Valley of California. Cleveland and Kleiner (7) found higher ozone concentrations when air was flowing from the Camden-Philadephia urban complex to remote sites 27 to 49 km distant. Nitigan et al. (3), working in the Ohio Valley in the summer of 1974, found the NAAQS to be exceeded twice as frequently at the rural sites as at the urban sites. They and others (11,18) also support that transport of ozone precursors from urban areas to rural areas occurs under appropriate meteorological conditions.

The present study was initiated to identify oxidant symptom patterns on white pine in the mountainous areas of southwestern Virigina. Study of weather patterns associated with various oxidant levels was also conducted.

MATERIALS AND METHODS

From April 1975 through April 1976 continuous monitoring took place at three rural sites in Virginia: (1) Salt Pond Mt., Giles County; (2) Rocky Knob Mt., Floyd County.; and (3) Shenandoah Valley, Rockingham County. In May of 1976, Station 3 was relocated to Apple Orchard Mt. in Bedford County. Total oxidant has been monitored with 1% buffered potassium iodide (KI) calibrated Mast Meters (Model 724-2) located within the U.S. Weather Bureau station structures.

At the Salt Pond Mt. site 21 trees within a 15-year old white pine stand were grouped into one of three symptom classes (sensitive, intermediate, tolerant) with seven trees per class. Sensitive trees were characterized by stunted tree growth and short needles with tip burn and chlorotic mottle symptoms; only current-year needles were present. Intermediate trees had longer needles with chlorotic spots and mottling symptoms; only current-year needles were present. Tolerant trees had long green needles that were symptomless; two year old needles were present. In May of 1976 six additional trees located near Site 2 were added to the study.

After candle elongation and fasicle emergence in late May 1975 and 1976, one branch was randomly selected on each tree and 12 faciles on the branch terminal and one lateral were selected and marked. Four fasicles were marked on the bottom, middle, and top of each candle in sequence.

All needles on all fasicles were rated for seven symptom types at approximately 11-day intervals during the growing season. Symptom expression was rated according to the following scale: (1) chlorotic spot; (2) chlorotic mottle; (3) chlorotic band; (4) chlorotic tip; (5) necrotic spot; (6) necrotic band; (7) tip burn. The severity index was computed by multiplying the number of the symptom by the percent injury. All symptoms were observed during the study period.

During the 1976 field season a system for evaluating total tree response to oxidant exposure was introduced. This symptom was modeled after that used by Miller (14) in the San Bernardino Mountains. Trees were rated quantitatively in both upper and lower crown for needle retention, condition, and length. Possible scores ranged from 0 to 9 for sensitive, 10 to 14 for intermediate, and 15 to 18 for tolerant trees. The total tree evaluation system was used to rate the aforementioned 21 field trees at Salt Pond Mt. along with 28 new trees on the Blue Ridge Parkway between Rocky Knob and Apple Orchard Mt., a distance of approximately 145 km.

RESULTS

1975: For a portion of the study period, May to August 1975, the hourly oxidant concentration was 4.27, 4.96, and 3.15 pphm for Sites 1, 2, and 3, respectively. On July 3, 1975 all three sites recorded oxidant levels above the NAAQS (Figure 1). Throughout this period increases in oxidants were associated with winds from the NE and stationary high pressure systems. Decreases in oxidants were associated with passage of cold fronts from the NW, warm fronts from the S, and high winds from the SW.

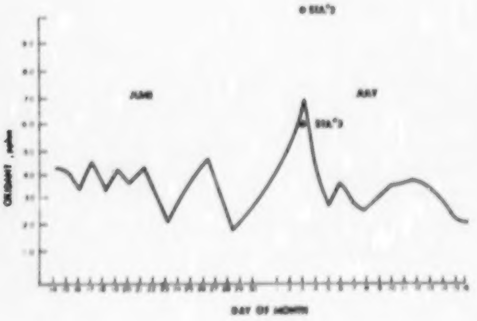

Figure 1. Oxidant in pphm (24 hr average) recorded at three monitoring sites in southwestern Virginia for the period June 14 to July 16, 1975.

The July 1-5 episode was experienced because of a low pressure system (hurricane Amy) being off the Atlantic Coast adjacent to New York. A high pressure system had moved down from Canada and was stationary over the Great Lakes states. The air circulation around a low pressure system is counterclockwise and clockwise around a high pressure system. On July 2 this pattern remained the same, forcing air from the NE south into Virginia (Figure 2). By July 3 the low pressure system had dissipated; the high pressure system had moved to Virginia, allowing for further oxidant synthesis as is characterized under these conditions. On July 4 a cold front originating over Canada passed over Virginia forcing the air of July 2 and 3 off the Atlantic Seaboard.

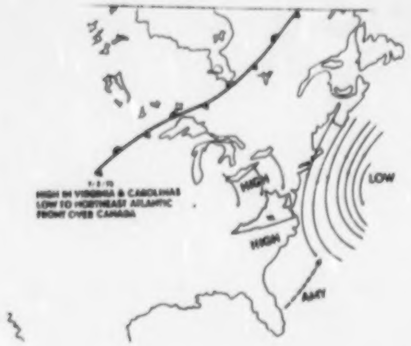

Figure 2. Weather map of meteorological conditions leading to the oxidant episode of July 3 and 4, 1975 in southwestern Virginia.

From July 1 to July 10 the mean severity index of needle injury of the Site 1 field trees increased from 105.59 to 197.83 for the sensitive, 2.27 to 32.92 for the intermediate and from 0.41 to 0.64 for the tolerant. The high levels of oxidant of July 3 resulted in a postemergence acute tipburn to white pine at all three sites (Table 1).

1976: Site averages of oxidant for the period April through July 1976 were 5.56 and 5.42 for Sites 1 and 2 respectively (Site 3 was not relocated until late May). The occurrence of increases and decreases of oxidant levels in response to weather conditions corresponded well with the 1975 findings.

June 4th marked the onset of an extended episode and from June 5 through 13 oxidant levels above the NAAQS were observed at all three stations for 110, 186, and 122 consecutive hours at Sites 1, 2, and 3 respectively. The same sites recorded 189, 186, and 134 consecutive hours above 6.0 pphm oxidant during this period (Figure 3a).

TABLE 1. SYMPTOM EXPRESSION OF WHITE PINE DUE TO OXIDANT LEVEL

Tree Class	June 20	July 1	July 10	July 21	
1975					
Tolerant	.21	.41	.64	.91	
Intermediate	1.61	2.02	32.82	34.24	
Sensitive	65.63	105.59	197.83	227.16	
	June 22	July 2	July 12	July 22	July 31
1976					
Tolerant	0.0	0.0	0.0	0.0	0.0
Intermediate	1.08	1.28	13.71	19.60	24.45
Sensitive	25.21	40.80	102.64	105.74	109.58

The June 5th through 12th episode resulted from winds out of the NE on the 5th and 6th and a stationary high pressure system that continued through the 12th. The 8th through the 10th had little to no air movement with increasingly clearer skies. On the 11th and 12th, winds were again out of the NE and the high pressure system persisted. The 13th and 14th brought the episode to a close; winds were out of the S and the high pressure system dissipated (Figures 3b-3j).

Oxidant injury to the field trees as recorded during the summer of 1976 at Site 1 is recorded in Table 1. From July 2 to July 12 the mean severity index of needle injury increased from 40.80 to 102.64 for the sensitive, 1.28 to 13.71 for the intermediate. Similar increases in oxidant injury were not observed on the tolerant trees at Site 2.

At Site 1, the total tree evaluation system showed a marked decrease in total scores (increased symptoms) for the sensitive and intermediate trees. There was an average decrease of 11% for sensitive and 12% for intermediate trees. The tolerant trees showed less than 1% decrease in total score for the period June 10 through July 31. For the same period, the white pines

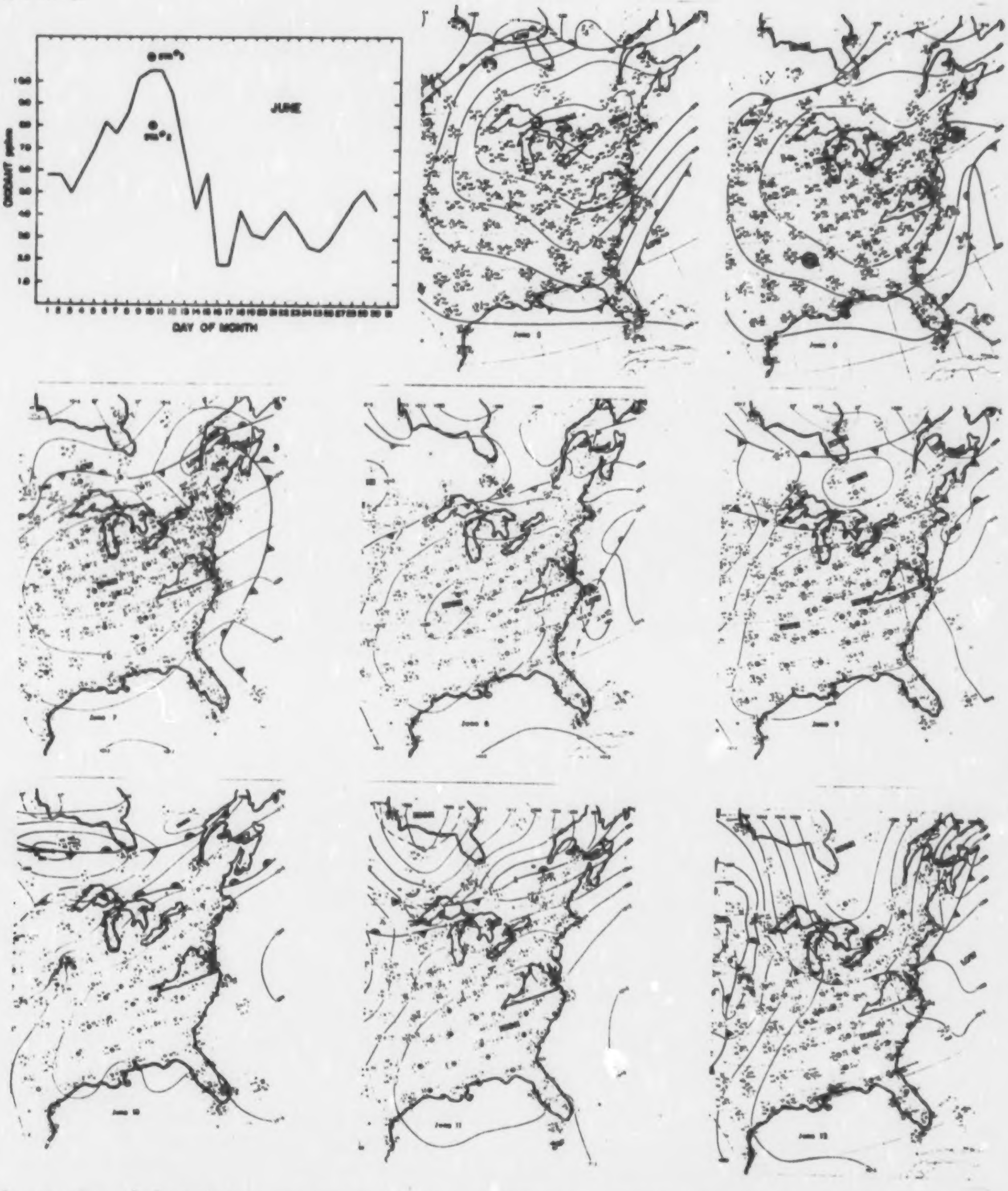

Figure 3. (a) Oxidant in pphm (24 hr average) recorded at three monitoring sites in southwestern Virginia for the period of June 1-31, 1976. (b-j) Weather maps of meteorological conditions during the oxidant episode of June 5-12, 1976.

along the Blue Ridge Parkway also showed a decrease in total tree score. There was an average decrease of 37.5% for sensitive, 22% for intermediate, and 10% for tolerant trees.

DISCUSSION

Data before the mid 1960's indicate that such high levels of oxidant were not previously observed in rural environments (5,12). While working in southwestern West Virginia in 1962, Berry (5) recorded levels 2 to 3 times less than those recorded in 1975 (Figures 4a-4b); note the similarity in diurnal oxidant patterns. Berry (personal communication, 1976) indicated that his Mast Ozone Meters were corrected using 2% buffered KI along with air flow calibration techniques. Therefore, the observed increased level of oxidant should be considered as reasonable estimates while taking into account site location and year to year variation. The high levels of oxidant reported in this study confirm the findings of other researchers (1,2,3,7,8,9,13).

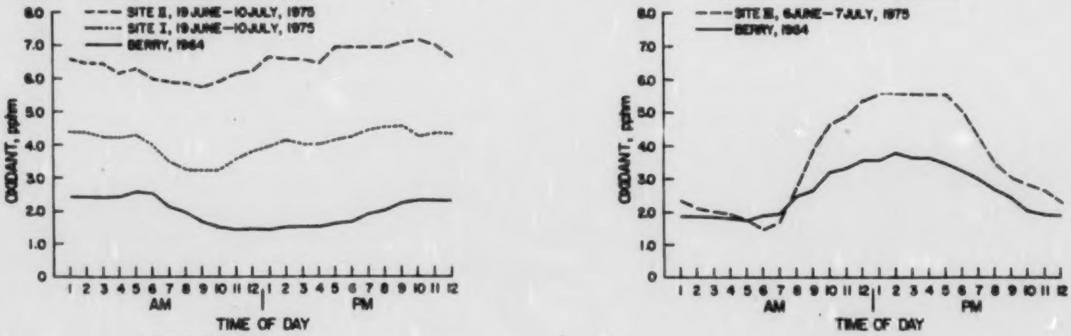

Figure 4. (a) Comparison of 1962 oxidant levels as recorded by Berry (5) and 1975 oxidant levels as recorded at two moutain locations in southwestern Virginia. (b) A similar comparison valley sites 1964 vs. 1975. Locations were different, monitoring dates were identical.

The data collected in our study further indicate transport of oxidant and oxidant precursors from the urban environment to the rural environment under appropriate meteorological conditions. Moreover, under centain conditions high levels of pollutants can be transported several hundred miles as is the case reported here. Under the influence of the determinate meteorological conditions preceeding July 3, 1975, it is probable that air pollutants were transported into southwestern Virginia from areas as far away as New York City. This is not a new phenomenon. On July 2, 1974, the air was moving the opposite direction, to the NE and high levels of ozone were transported into Connecticut and Massachusetts from New York City (8). Under adverse conditions, the oxidant levels in southwestern Virginia are influenced by the urban environment as was shown by the association of oxidant increases and winds from the northeast.

Increases in oxidants during the investigation were also observed under high pressure systems. The weather conditions occurring during the episode of June 1976, were winds out of the NE and an associated high pressure system. High pressure systems were characterized by disorganized wind patterns and clear to partly cloudy skies. Under these conditions, there is no movement of air from a given geographical region and photochemical generation of oxidants is increased.

It has been hypothesized that the type of reactions generating oxidants in the rural atmosphere are similar to those generating oxidants in the urban atmosphere (16,17). However, natural synthesis alone in the rural environment could not singly account for the levels of oxidants being reported. The urban reaction system has a far greater emission intensity of oxidant precursors that are responsible for the undesirable effect of photochemical smog.

The urban reaction system is more likely the contributor of stable intermediate precursors that would contribute to oxidant synthesis in the rural environment. Photochemically, oxidants are generated by the reaction of oxides of nitrogen (NO_x) and hydrocarbon (HC) (18). High levels of oxidants are generated when NO is depleted in the presence of sunlight. As air moves from the urban to the rural environment, the HC to NO_x ratio increases. As this ratio increases, the oxidant dosage increases (11). This appears to be the case in the rural environment. If these premises are correct, then we are dealing with a photochemical oxidant generation system in southwestern Virginia that is highly dependent on the sun's energy and should show systematic increases and decreases over large geographical regions. This is the case in southwestern Virginia.

The increase in symptom severity index observed on July 10, 1975 was sixteen fold for the intermediate trees. This appeared within one week of the episode peak. This would seem to indicate a direct response to the high levels of oxidant occurring July 3 and 4.

The increase in symptom severity index recorded on July 12, 1976 was elevenfold for the intermediate trees. This was recorded approximately four weeks after the June episode. Symptom development has not been observed to require as long as 4 weeks following acute exposure, and this leads us to believe that this symptom expression may be an accumulative oxidant response, indicating a low dose over time.

Both the 1975 and 1976 increases in symptom expression were observed during the 2nd week in July. Berry (6) noted tissue age as a factor in symptom expression. Assuming needle extension to occur at about the same time in 1975 and 1976, one could correlate this increased expression to the age of the needle tissue at the time of dosage.

The total tree evaluation system indicated a decrease in average tree scores (increase in symptoms) at both Site 1 and along the Blue Ridge Parkway. The trees along the Parkway showed a greater increase in symptoms than did the others. This could indicate the presence of higher oxidant levels in the Blue Ridge versus the southern Appalachian Mountains. Age could also be a factor; the trees along the Parkway were mature while those rated at Site 1 were part of a 16-year-old stand. The sample along the Parkway included only one sensitive tree. This may explain the particularly large decrease (37.5%) in the average sensitive tree score there.

Severe damage to white pine has been observed in this study and statistical analysis has significantly correlated the 1975 damage with increased oxidant concentration during specific time intervals.

CONCLUSION

Oxidant levels were monitored for 15 months and distinct weather patterns were correlated with high levels in the mountainous areas of southwestern Virginia. Winds out of the NE were involved in all pollution episodes. While symptom development on native and planted white pines continued throughout the entire growing season, definite increases in severity were associated with the occurrence of an episode of oxidant increase.

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THE EFFECTS OF OZONE ON PLANT-PARASITIC NEMATODES AND CERTAIN PLANT-MICROORGANISM INTERACTIONS

D. E. Weber*

ABSTRACT

The influence of air pollutants on parasitism of soybean by soil nematodes with different feeding habits was studied. Soybean was exposed to 0.25 microliter/liter ozone (O_3) and sulfur dioxide (SO_2), singly and in mixture, and to charcoal-filtered air. Plants were exposed for 4-hour periods prior to nematode inoculations and on 3 days/week after inoculation until experiments were terminated. At 36 and 67 days after inoculation, reproduction of the soybean cyst nematode (Heterodera glycines) was inhibited by exposure of nematode-infested plants to O_3 and the O_3-SO_2 mixture. The effects of these pollutants influenced the reproduction of cyst nematodes by suppressing populations of both female and male nematodes, and the total number of eggs and larvae. Treatment of soybean with O_3 and the O_3-SO_2 mixture, greatly suppressed the reproduction of stubby root nematodes (Trichodorus christiei). Reproduction of sting nematodes (Belonolaimus longicaudatus) was usually not affected by the pollutants. The growth of nematode-infested soybeans was inhibited by O_3 and the O_3-SO_2 mixture. Formation of root nodules on soybean inoculated with sting and stubby root nematodes was also suppressed by O_3 and the O_3-SO_2 mixture when compared with the control. Nodulation of soybean inoculated with the cyst nematode was not affected by the pollutants.

Injury of begonia foliage by a single 4-hour exposure to O_3 and a O_3-SO_2 mixture at 0.25 microliter/liter appeared to suppress the reproduction of the foliar nematode (Aphelenchoides fragariae). Plants were exposed to the pollutants before and after nematode inoculations. Foliar injury resulting from O_3 and the O_3-SO_2 mixture prior to inoculation was associated with a pronounced suppression of nematode reproduction.

INTRODUCTION

Oxidants and other air pollutants injure plant foliage and inhibit the growth and productivity of plants. Air pollutants also affect interactions involving vegetation and microorganisms (1,2). Field and laboratory investigations have shown that ozone (O_3) influences interactions involving fungi, bacteria, and viruses associated with a large number of plants (Table 1). These effects range from an increase in the infection of plants by such pathogens as Botrytis cinerea (3) and Fomes annosus (4) to an inhibition in the

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TABLE 1. THE EFFECT OF OZONE ON INTERACTIONS INVOLVING PLANTS AND MICROORGANISMS

Organisms	Experimental conditions	Ozone concentration	Effect	Reference
FUNGI				
Fungi on:				
leaves of pinto bean	greenhouse	.06 μl/l, 8hr/ day, 28 days	Increased number of fungi	14
roots of pinto bean	greenhouse	.1-.15 μl/l,8hr/ day, 4-28 days	Same	8
Botrytis on:				
potato	greenhouse	.15-.25 μl/l 6-8 hr	Increased severity & deveopment of disease	3
potato	field	ambient air	Same	3
geranium	greenhouse	.07-.1 μl/l 10 hr/day 15-30 days	Increased infection on injured leaves	15
broad bean	greenhouse	.20 μl/l, 8 hr	Less foliar injury by O_3 on leaves	16
Fomes annosus on ponderosa pine	field	ambient air	Colonization by fungus increased	4
Fusarium in tomato	greenhouse	.06-.08 μl/l 6 hr/day,5 days/ wk, 45 days	Suppressed plant growth and delayed wilt symptoms	17
Puccinia on:				
oats	greenhouse	.1 μl/l, 6 hr/ day, 10 days	Inhibited fungal growth	5
wheat	growth chamber	.06 μl/l,6 hr/ day, 3-17 days	Inhibited fungal growth & spore production	6
		.06 μl/l, 6 hr	Infection inhibited	6
wheat	growth chamber	.30 μl/l, 5 hr	Protected areas of leaves from O_3 injury	18
Uromyces on pinto bean	greenhouse	ozonated olefins .4-.5 μl/l, 3 hr	Same	11

(continued)

Table 1 (continued)

Organisms	Conditions	Concentration	Effect	Reference
Erysiphe on:				
barley	growth chamber	.05 µl/l,6 hr/ day, 3 days	Leaf infection by condia inhibited	19
		6 hr/day for 2 days	Fungal growth inhibited	19
		6 hr/day, more than 2 days	Fungal growth enhanced	19
Aureobasidium on white pine	growth chamber	.07 µl/l 4.5 hr	Fungus on leaves injured by O_3 only	20
Lophodermium on white pine	growth chamber	.07 µ/l 4.5 hr	No effect on colonization of host	20
BACTERIA				
Pseudomonas in:				
soybean	growth chamber (?)	.25 µl/l, 4 hr	Fewer bacterial lesions	7
kidney bean	greenhouse	.60 µl/l, 1 hr	Areas near lesions protected from O_3 injury	12
Rhizobium nodules on:				
pinto bean	greenhouse	.1-.15 µl/l, 8 hr/day, 4-28 days	Nodules absent	8
Lee soybean	greenhouse	.75 µl/l, 1 hr	Lower numbers and weights of nodules	9
soybean	greenhouse	.12 µl/l 5 days/wk, 3 wk	Fewer nodules	10
VIRUSES				
Bean Common mosaic in bean	growth chamber	.25 µl/l, 4 hr	Inhibited development of O_3 injury of leaves	21
	field	ambient air	Same	21
Tobacco etch in tobacco	growth chamber	.25 µl/l, 4 hr	Same	22
Tobacco mosaic virus in:				
tobacco	growth chamber	.30 µl/l, 3-6 hr	Same	13
pinto bean	growth chamber	.10 µl/l, 3 hr	Increase in number of viral lesions	23

development of rust fungi (5,6), and a bacterial pathogen (7). The results of several studies have indicated that root nodule formation by nitrogen-fixing bacteria is inhibited when leguminous plants are exposed to O_3 (8,9,10). In other research, microorganisms have been implicated in the protection of leaf tissues from O_3 injury (11,12,13).

Research involving the effects of O_3 on plant and microfauna associations has not been found. Plant-parasitic nematodes were utilized to study the effects of O_3 on one aspect of plant and microfauna interactions.

Nematodes comprise a group of about 500,000 species. They are present in soil and aquatic environments in large numbers. Some are important parasites of plant and animals. Many feed on microorganisms and decaying materials. They transport bacteria and fungi within the rhizosphere and are involved in the dissemination of plant pathogens. Nematodes provide a source of nutrients for organisms and may be involved in the mineralization of organic matter (24, 25). This paper reports the results of one study to determine the influence of O_3, singly and in a mixture with sulfur dioxide (SO_2), on soil and foliar plant-parasitic nematodes.

PROCEDURES

SOIL NEMATODES

The parasitism of soybean [Glycine max L. (Merr.) 'Dare'] by soil nematodes was investigated in greenhouse facilities. Seedlings of soybean were grown from seed in sand. Roots were inoculated with a commercial inoculum of nitrogen-fixing bacteria (Rhizobium japonicum). Seedlings were then exposed to 0.25 microliter/liter O_3 and SO_2, singly and in mixture, and to charcoal-filtered air in 12.5 m^3 exposure chambers. Four-hour exposures were made within a 1-week period prior to nematode inoculations and on three alternate days/week after inoculation until experiments were terminated. Three to five plants were utilized in each treatment.

Fifteen days after planting, soybean seedlings were inoculated with nematodes. The data summarized in this paper are from single experiments, involving both endo- and ectoparasitic species. Similar results were observed in replications of these experiments. In experiments involving a sedentary endoparasite, roots of test plants were inoculated with 9000 eggs per plant of the soybean cyst nematode (Heterodera glycines). Two ectoparasites were studied in related experiments. In these experiments, roots of soybean were inoculated with 400 sting (Belonolaimus longicaudatus) and 100 stubby root (Trichodorus christiei) nematodes per plant.

Soybean cyst nematode experiments were terminated 36 and 67 days after inoculation. Female cysts were washed from roots. Twenty cysts per sample were crushed to evaluate the production of eggs and larvae. Males were extracted from samples of sand (26). Nematodes and eggs were counted and values converted to per plant totals.

Experiments with sting and stubby root nematodes were terminated 48 and 79 days after inoculation. Population counts per plant were determined from sand samples.

FOLIAR NEMATODES

Schwabenland Red begonia was used in the evaluation of the effects of injury by O_3 and SO_2 on the foliar nematode, *Aphelenchoides fragariae*. Three begonia plants were exposed to each pollutant at 0.25 microliter/liter concentrations and to filtered air as described for one, 4-hour exposure period. Utilizing two groups of plants, pollutant exposures were conducted 3 days before leaves were inoculated with nematodes or 3 days after inoculation. Four leaves per plant were inoculated with 150 nematodes per leaf.

Thirty days after inoculation, nematodes were extracted from leaves and counted from diluted samples. The amount of injury on each inoculated leaf was estimated on a 0 to 100% scale 3 days after exposure of each plant group and 30 days after inoculation.

RESULTS AND DISCUSSION

The influence of O_3 and the O_3-SO_2 mixture on the soybean cyst, stubby root, and foliar nematodes was inhibitory. This inhibition was probably caused by a suppression in the growth of the host, foliar injury, and various metabolic changes associated with the host-parasite-pollutant interaction. The effect of SO_2 alone on nematode populations, plant weights, and the formation of nodules was similar to the control.

EFFECTS ON SOIL NEMATODES

The inhibitory effects of O_3 and the O_3-SO_2 mixture were first observed 36 days after inoculation, where the number of female cysts/plant was slightly lower than the control. At 67 days, the inhibitory effect was much larger and amounted to a 73 to 77% suppression in the number of cysts/plant as compared with the control. Treatment of soybean with O_3 and the O_3-SO_2 mixture also inhibited the production of male nematodes and the total number of eggs and larvae (Table 2).

Damage of soybean by O_3 and the O_3-SO_2 mixture may have depressed the quantity and quality of organic and inorganic substances. Since the growth of shoots and roots was inhibited by these pollutants (Figure 1), the chemical constituents of soybean were probably altered. These substances are utilized by nematodes in the establishment of a feeding relationship with the host. If plant chemistry is modified, the growth and reporduction of nematode populations may be impaired. Tingey (27) discussed various mechanisms that may be involved in ozone-induced modifications of the chemistry of roots and foliage. In addition, the production of toxins in roots of plants damaged by O_3 and the O_3-SO_2 mixture may have influenced the growth of nematode populations.

Formation of nodules in roots of soybean by nitrogen-fixing bacteria was not affected by the pollutants. The effects of the pollutants on nodulation

TABLE 2. INFLUENCES OF O_3 AND SO_2 ON THE SOYBEAN CYST NEMATODE AT 67 DAYS AFTER INOCULATION

	Numbers per plant		
Treatments	Females (Cysts)	Males	Eggs and larvae
Control	1,955	2,656	146,013
SO_2	1,738	2,239	112,220
O_3	525*	356*	43,573*
Mixture	451*	555*	46,321*

*Significantly different from the control at P=0.05.

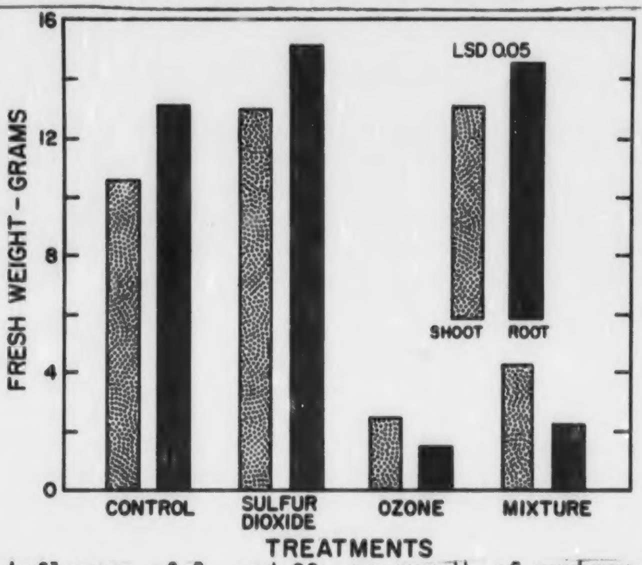

Figure 1. The influence of O_3 and SO_2 on growth of soybean infected with soybean cyst nematodes.

were probably masked by the severe inhibition of this process by soybean cyst nematodes (28).

Since O_3 is highly reactive, it is doubtful that this pollutant would have a direct effect on soil organisms. This has been confirmed in experimentation which demonstrated that O_3 does not pass through sand, peat, and gravel soil mixes.

The influence of O_3 and the O_3-SO_2 mixture on the two ectoparasites was different. Population counts of sting nematodes were usually not significantly affected by exposure of soybean to the pollutants. However, the exposure of soybean to O_3 and the O_3-SO_2 mixture greatly inhibited the stubby root nematode.

This inhibition was observed at 48 and 79 days after inoculation and ranged from 72 to 91% of the control (Table 3).

The growth of soybean infested with the ectoparasites and the formation of root nodules was suppressed by O_3 and the O_3-SO_2 mixture (Figure 2). These effects of the pollutants had little influence on the size of the sting nematode populations. The pollutants, however may have influenced reproduction of

TABLE 3. INFLUENCES OF O_3 AND SO_2 ON REPRODUCTION OF COMBINED POPULATIONS OF STING AND STUBBY ROOT NEMATODES ON SOYBEAN

Treatments Days after inoculation	Nematodes per plant Sting	 Stubby root
Control		
48	2,794	19,748
79	14,029	25,547
SO_2		
48	2,428	16,190
79	11,009	23,604
O_3		
48	2,802	3,589*
79	11,276	7,051*
Mixture		
48	2,130	1,791*
79	9,244*	4,010*

* Significantly different from the control at $P=0.05$.

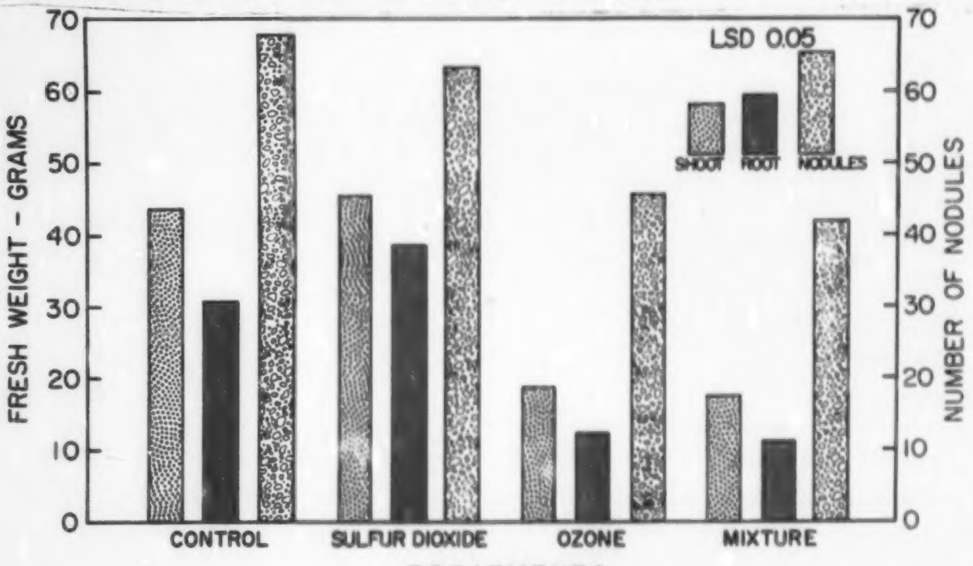

Figure 2. The influence of O_3 and SO_2 on growth and nodulation of soybean infected with populations of sting and stubby root nematodes.

the stubby root nematode by inhibiting the development of root tips. Since root tips are more suitable feeding sites for this nematode than other root regions (29), a decline in the number of apical areas could limit nematode feeding and reproduction. The sting nematode is less specific with regard to feeding sites (30).

EFFECTS ON THE FOLIAR NEMATODE

Injury of begonia leaves by O_3 and the O_3-SO_2 mixture appeared to inhibit the reproduction of the foliar nematode. This inhibition was associated with leaf injury induced by O_3 and the O_3-SO_2 mixture within 3 days after the exposure of plants to the pollutants. Injury resulting from the infection of leaves by nematodes during the 30-day period following inoculation also probably contributed to the inhibitory response. The inhibition of nematode reproduction was greater when plants were exposed to O_3 and the O_3-SO_2 mixture before inoculation with nematodes than when plants were exposed to the pollutants after inoculation (Table 4). The deviation in the amount of injury within the two inoculation treatments was probably the result of differences in environmental conditions (light, temperature, humidity) associated with the exposure periods, rather than a protective effect by the presence of nematodes.

TABLE 4. RESPONSES OF BEGONIA AND THE FOLIAR NEMATODE TO O_3 AND SO_2

Treatments	Leaf injury (% leaf) 3 days*	Leaf injury (% leaf) 30 days#	Number of nematodes/leaf
Before inoculation			
Control	0	48	43,700
SO_2	0	50	38,950
O_3	77	86	9,000
Mixture	68	75	13,400
After inoculation			
Control	0	48	45,100
SO_2	0	58	43,300
O_3	58	72	34,500
Mixture	38	61	27,900
Standard Error	4	6	5,200

* Injury was estimated on a scale of 0-100% at 3 days after exposure.

# Injury estimated on a scale of 0-100% when nematodes were extracted from leaves, at 30 days after inoculation.

The inhibitory effects on nematode reproduction were probably related to the destruction of nematode-feeding sites and conditions that made begonia leaves less suitable as a host for this nematode.

CONCLUSIONS

These studies have provided an evaluation of the effects of O_3, alone and combined with SO_2, on the plant-parasitic association of both soil and foliar nematodes. Previous investigators demonstrated that many types of plant-parasitic associations, involving fungi, bacteria, and viruses, are influenced by O_3. These investigations have shown that an additional type of plant-parasitic association, involving nematodes, is also influenced by O_3. In parasitic associations, O_3 has been found to inhibit or enhance the development of microorganisms on plants. Most results indicate that the effect probably involves an ozone-induced modification in the susceptibility of the host or, in some cases, a change in the pathogenicity of the microorganism.

There is a need to examine the broader aspects of these associations. Microorganisms are required in the decomposition of organic matter. The association of saprophytic fungi with foliage and roots have been examined in only a few studies. In these studies, the number of fungi was increased by exposure of plants to O_3. The increase appeared to be related to the presence of injured tissues. However, in laboratory studies, O_3 was found to inhibit several saprohpytic microorganisms. Oxidants and other pollutants may directly interfere with the growth of microbial populations associated with the process of decomposition. In other instances, the inhibitory effects of oxidants on photosynthesis, plant growth, and other physiological processes may influence decomposition by suppressing the availability of organic materials. By interfering with decomposition, O_3 could alter the normal cycling of nutrients within ecosystems. Other microbial processes are important components of ecosystems. The suppressive effects of O_3 on the formation of root nodules by nitrogen-fixing bacteria may reduce usable forms of nitrogen. Also a disruption in the mycorrhizal association of fungi and plant roots could inhibit plant nutrition.

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SESSION 13

EFFECTS OF OXIDANTS ON VEGETATION - II

Chairman: W.W. Heck
North Carolina State University at Raleigh

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GROWTH REPONSE OF CONIFER SEEDLINGS TO LOW OZONE CONCENTRATIONS

R. G. Wilhour and G. E. Neely*

ABSTRACT

Juvenile seedlings of Jeffrey pine (Pinus jeffreyi Grev. and Balf.) Monterey pine (P. radiata D. Don), shore pine (P. contorta var. contorta Dougl. ex Laud), lodgepole pine (P. contorta var. murrayana [Balf.] Critchf.), sugar pine (P. lambertiana Dougl.), western white pine (P. monticola Dougl.), ponderosa pine (P. ponderosa Laws.), Sitka spruce (Picea sitchensis [Bong.] Carr.) and Douglas fir (Pseudotsuga menziesii [Mirb.] Franco.) were exposed to a standardized daily ozone (O_3) dose (an average of 10 pphm (200 $\mu g/m^3$), six hours per day) seven days per week in outdoor exposure chambers. Controls were treated with charcoal-filtered ambient air. Pots were placed under the experimental treatments immediately following seeding and remained there up to 22 weeks.

Growth response of the nine conifer species was evaluated following 18 continuous weeks of exposure to O_3. Significant growth reductions related to the O_3 treatment were relatively consistent only for ponderosa pine and western white pine. Significant growth reductions (given as % reduction from control) were observed in root length (12.1%)*, dry weight (DW), stem (21.3%)*, and DW root (26.3%)** of ponderosa pine and DW foliage (12.9%)** and DW stem (9.1%)* in western white pine. The proportion of total foliar surface injured on ponderosa pine exposed to O_3 was relatively high (20%) but practically absent on western white pine (1%). No constant relationship between foliar injury and growth response to O_3 was observed between species. The relative foliar injury response of the conifers was ponderosa pine (20%), lodgepole pine (16%), shore pine (13%), Jeffrey pine (2%), Douglas fir (1%), sugar pine (1%), western white pine (1%), Sitka spruce (1%), and Monterey pine (0%). Tip necrosis or chlorosis were the most common symptoms of O_3 injury to primary needles; typical chlorotic mottling was observed on a few secondary needles of ponderosa pine.

The effect of O_3 on ponderosa pine seedling emergence was examined by counting the number of emerged seedlings in O_3 and control treatments on a biweekly schedule beginning two weeks after seeding. Significant** differences in seedling emergence between treatments first appeared four weeks after seeding. At the termination of the emergence experiment, a greater number of seedlings had appeared in the O_3 treatment.

Ponderosa pine seedlings were additionally exposed to the standardized

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*daily O_3 dose for 0, 1, 2, 3, 4, 5, 6, or 7 days per week for 18 continuous weeks. Only DW stem (16%) was significantly** reduced from the control by O_3; this difference was observed at the 6 (19%) and 7 (17%) days per week O_3 treatments. Foliar injury was slight between 0, 1, 2, and 3 days of O_3 exposure per week (averaged 2.4%) but increased markedly at exposures lasting 4 days per week or longer (averaged 17%).*

Biweekly harvests of ponderosa pine seedlings throughout a 20 week test period showed no statistically significant growth reductions in plant height or root length, and no differences were expected from further exposure to the O_3 dose used in this experiment. Highly significant treatment differences were not detected in DW top; however, a distinct trend of increased growth differences with increased exposure time was present. It is likely that significant treatment differences in DW top would occur at longer O_3 exposures. Root growth in dry weight was the most sensitive growth response of ponderosa pine to O_3. Significant treatment differences at the 98% confidence level were detected, and a trend of increased growth differences with increased exposure time to O_3 was evident. The DW root of the O_3 treatment was reduced 26% from the control; it is probable that this difference would be greater at longer exposures to O_3.

INTRODUCTION

Experiments on the response of tree species to O_3 vary in experimental hardware but often share characteristics such as relatively high pollutant concentrations and single, short exposures. Visual estimates of foliar injury are frequently used to evaluate tree response to such pollutant regimes. The results of such experimentation include determination of species sensitivity to O_3 (3,9,23,24), O_3 dose and injury response relationships (11, 16), threshold O_3 concentrations required to cause foliar injury (23), effects of age or season or environmental factors on sensitivity (7, 9, 10, 11), relative toxicity of gaseous pollutants (3), and pollutant interactions (8, 13).

Quantification of growth or physiological response of trees to pollutants provides more reliable conclusions than estimated % foliar injury and is often more directly related to economic or ecological factors. Quantitative data on tree response to O_3 to date include the effects of O_3 on net photo-synthetic rates (5) and foliar and height growth rates (13, 15, 21).

Analyses of ambient air show that vegetation is exposed to dynamic patterns of oxidant concentrations rather than single exposures at fixed, relatively high concentrations (6, 17, 20). Simulated ambient O_3 exposures should include a 24 hr. O_3 concentration periodicity plus repeated exposures throughout growing seasons. Simulated ambient O_3 exposures followed by detailed growth and physiological assessments sharpen the appraisal accuracy of the response of wood vegetation to O_3. Response of tree species to chronic O_3 exposures approximating ambient O_3 conditions has been investigated by a few scientists. Physiological (1, 2, 18, 22) and growth (14) responses were measured.

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* Significantly different at 90% confidence level.
**Significantly different at 95% confidence level.

This research was designed to investigate the relative growth response of several forest tree species to low O_3 doses applied over a long time and to intensively investigate the growth of a selected tree species growing under such a pollutant schedule.

METHODS AND MATERIALS

Nine western conifer species (Jeffrey pine, Monterey pine, shore pine, lodgepole pine, sugar pine, western white pine, ponderosa pine, Sitka spruce, and Douglas fir) were used in the study. Seeds were stratified four weeks at 5°C. and planted in Jiffy-Plus potting medium contained in 10 x 30 cm high pots. Four seeds were arranged at each of four predetermined locations in each pot and covered with 3-4 mm potting medium. A total of 496 pots of ponderosa pine and 36 each of the remaining eight species were evenly assigned to six outdoor exposure chambers (12). Species and treatments were randomly located in six blocks within each test chamber. The experimental treatments commenced immediately after seeding in mid-June and continued into November.

Ozone produced by irradiating charcoal-filtered ambient air with high intensity ultraviolet light was maintained in three test chambers an average of 10 pphm (200 $\mu g/m^3$), six hrs. per day (9:30 am-3:30 pm) and seven days per week for 22 weeks. The O_3 concentrations were allowed to follow a pattern of low (8±1 pphm) in the morning hours and gradually increasing to 12±1 pphm later in the day. Ozone concentrations were continuously monitored with Mast meters (Mast Development Co., Ames, Iowa) calibrated weekly with a MEC 1000 ozone calibrator (McMillan Electronics Co., Houston, Texas). The MEC calibrator was periodically compared to the standard 1% neutral-buffered potassium iodide method. Charcoal-filtered ambient air was passed into three remaining chambers that housed control plants.

SEEDLING EMERGENCE

The effects of the O_3 treatment on the emergence of ponderosa pine seedlings were evaluated by counting the number of emerged seedlings on a biweekly schedule for six weeks. All treatments were analyzed that included exposure of ponderosa pine to the standardized daily O_3 dose (10 pphm, six hrs. per day) seven days per week for six weeks; appropriate controls were also observed. The first observation was two weeks after seeding. The few seedlings that emerged after the six week observation period were not included in the emergence data.

Seedlings were thinned on the same biweekly schedule referred to above. The four most uniform seedlings per container were retained, one at each of the predetermined positions.

SPECIES SENSITIVITY

Growth of the nine species to O_3 was evaluated in mid-November following 20 continuous weeks of exposure to O_3. The seedlings were carefully removed from the potting medium and roots were washed clean with tap water. Root length was measured as the distance between the root collar at soil level and the primary root tip. Plant height was measured as the distance between the cotyledons and the tip of the apical bud. Foliar injury response was approximated by estimating the percent of the foliar surface area injured.

Stems, roots, and foliage were bagged separately by four plant (pot) samples and dried at 70°C for 72 hrs; dry weights (DW) were recorded. All response parameters were recorded as a four plant (pot) average.

VARIABLE O_3 TREATMENT

Effects of variable O_3 exposure durations on ponderosa pine were tested by rotating 18 pots per treatment weekly between treatments. Seedlings were effectively exposed to the standardized daily O_3 dose for 0, 1, 2, 3, 4, 5, 6, or 7 days per week for 18 continuous weeks. The response parameters referred to earlier were measured at the termination of the study. The statistical treatment of the data in this study and the previous study included an analysis of variance and an F-test to detect treatment differences at the 90, 95, or 99% confidence level.

PONDEROSA PINE GROWTH

The growth response of ponderosa pine seedlings over time to the daily O_3 schedule referred to earlier administered seven days per week was estimated by biweekly harvests beginning two weeks following seedling emergence and ending 18 weeks later. The parameters measured were plant height, root length, DW top (stem + foliage), and DW root. The data were plotted and a non-linear least squares method was used to fit the curves. The growth curves of outside diameter (OD) top and OD root showed a divergence between treatments with successive harvests indicating that treatment differences would most likely appear at later harvests. The last four harvests, representing 14, 16, 18, and 20 weeks of exposure to O_3, were chosen for regression analysis. The 20 week treatment to O_3 in this experiment is identical to the O_3 treatment of ponderosa pine in the species sensitivity test.

RESULTS AND DISCUSSION

SEEDLING EMERGENCE

Results of the experiment on the influence of O_3 on seedling emergence demonstrated that rate of seedling emergence was affected by O_3 exposure. The number of seedlings emerged at the three observation periods was always greater in the O_3 treatment (Table 1). Significant differences in seedling emergence between treatments first appeared at four weeks after seeding (95% confidence level). At six weeks, seedling emergence in the O_3 treatment was higher than controls at the 90% confidence level.

How O_3 treatment caused an increase in both rate of ponderosa pine seedling emergence and total number of seedlings emerged cannot be inferred from this experiment. Blum and Tingey (4) demonstrated that O_3 did not pass through sand, peat, and gravel soil mixes; this suggests an indirect effect of O_3 on ponderosa pine seedling emergence. The effect may be related to altered soil chemical or microbiological components mediated by O_3 reacting with the surface layer of the potting medium.

SPECIES SENSITIVITY

Response of the nine test species to 20 weeks of treatment to the standardized daily O_3 dose (10 pphm for 6 hr) for 20 continuous weeks was evaluated in detail. Average growth and injury values are presented in Table 2. Ozone seriously injured foliage of ponderosa pine, lodgepole pine, and shore pine. The relative foliar response based on differences in % foliar injury between treatment and control plants was ponderosa pine (20%), lodgepole pine (16%), shore pine (13%), Jeffrey pine (2%), Douglas fir (1%), sugar pine (1%), western white pine (1%), Sitka spruce (1%), and Monterey pine (0%). Necrosis of needle tips was the predominant symptom of O_3 injury. Cotyledons and oldest primary needles were most severely affected. Chlorotic mottling occasionally occurred on secondary needles of ponderosa pine. The tip necrosis symptom in this study resembles that described by Davis and Wood (9) as occurring on primary needles of several conifers treated with acute O_3 exposures (25 pphm O_3 for eight hrs.); they also observed chlorotic mottle. A comparison of the results of the studies indicates that tip necrosis or chlorotic mottle may follow chronic or acute exposure of conifers to O_3. Neither symptom is, therefore, necessarily specifically related to chronic or acute O_3 exposures.

TABLE 1. EFFECT OF CHRONIC OZONE EXPOSURE ON SEEDLING EMERGENCE OF *Pinus ponderosa* Laws

Treatment	Time after seeding (weeks)	Emerged seedlings (number)	Germination (%)
Control	2	1279	37.0
	4	1457	42.2
	6	1516	43.9
Ozone	2	1299	37.6
	4	1545**	44.7
	6	1589*	46.0

* Significantly different from control at 90% confidence level (Chi Square test)

** Significantly different from control at 95% confidence level (Chi Square test)

Significant growth reductions occurred in ponderosa pine and western white pine. Significant growth reductions in ponderosa pine due to O_3 treatment were root length (12%)*, DW stem (21%)*, and DW root (26%)** (Table 2). In western white pine, DW foliage (13%)** and DW stem (9%)* were significantly reduced by the O_3 treatment. Interestingly, one of the two species showing significant growth reductions would be ranked very sensitive (ponderosa pine) based on foliar injury and the other (western white pine), resistant. Growth of other species showing a relatively high amount of foliar injury (lodgepole pine and shore pine) was not significantly affected by the O_3 treatment. Evidently visible injury is not a reliable predictor of growth response of conifer species to chronic O_3 exposures.

VARIABLE O_3 TREATMENTS

Because of the importance of ponderosa pine as a timber species and the knowledge already available on its O_3 sensitivity (18, 19), it was selected for detailed examination of response to O_3. Only stem DW was significantly** reduced from the control by the O_3 treatment and then only by exposures lasting six (19% reduction) or seven (17% reduction) days per week for the 18 week exposure period. In contrast, foliar injury response varied dramatically among O_3 treatments. Foliar injury remained constantly low (average 2.4%) at O_3 exposures of 0, 1, 2, and 3 days per week (Figure 1A). A pronounced increase in injury occurred when seedlings were exposed to O_3 for 4 to 7 days per week (average 16.5%). Significant growth reductions were not consistent with elevated foliar injury. Either foliar injury is a more sensitive response indicator of ponderosa pine to O_3 exposure or no consistent relationship exists between foliar injury (at the O_3 doses tested) and growth response. A similar disparity in O_3 sensitivity evaluations between growth and foliar sensitivity was also noted by Jensen (14) on deciduous tree species.

PONDEROSA PINE GROWTH

Sequential, biweekly harvests were taken throughout a 20-week growth period to examine growth response of ponderosa pine seedlings to the standardized daily O_3 dose for variable biweekly exposure increments of up to 20 weeks. The data were plotted and a non-linear least squares fit was used to fit the curve to the data. Each point on the growth curves (Figures 1B-1F) is the average value for 18 pots (72 seedlings). The growth patterns of plant height and root length were not obviously affected by the O_3 treatments (Figures 1B and 1C). Maximum growth was attained at 10 to 12 weeks following seedling emergence, regardless of treatment. Regression analysis of the last four harvests (14, 16, 18, and 20 weeks of exposure to O_3) showed no significant differences between treatments. Maximum plant height and root length were attained prior to the termination of the experiment; therefore, no further growth differences were expected between treatments if O_3 treatments had continued.

A regression analysis of DW top (stem + foliage) for the last four

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* Significantly different at 90% confidence level.

**Significantly different at 95% confidence level.

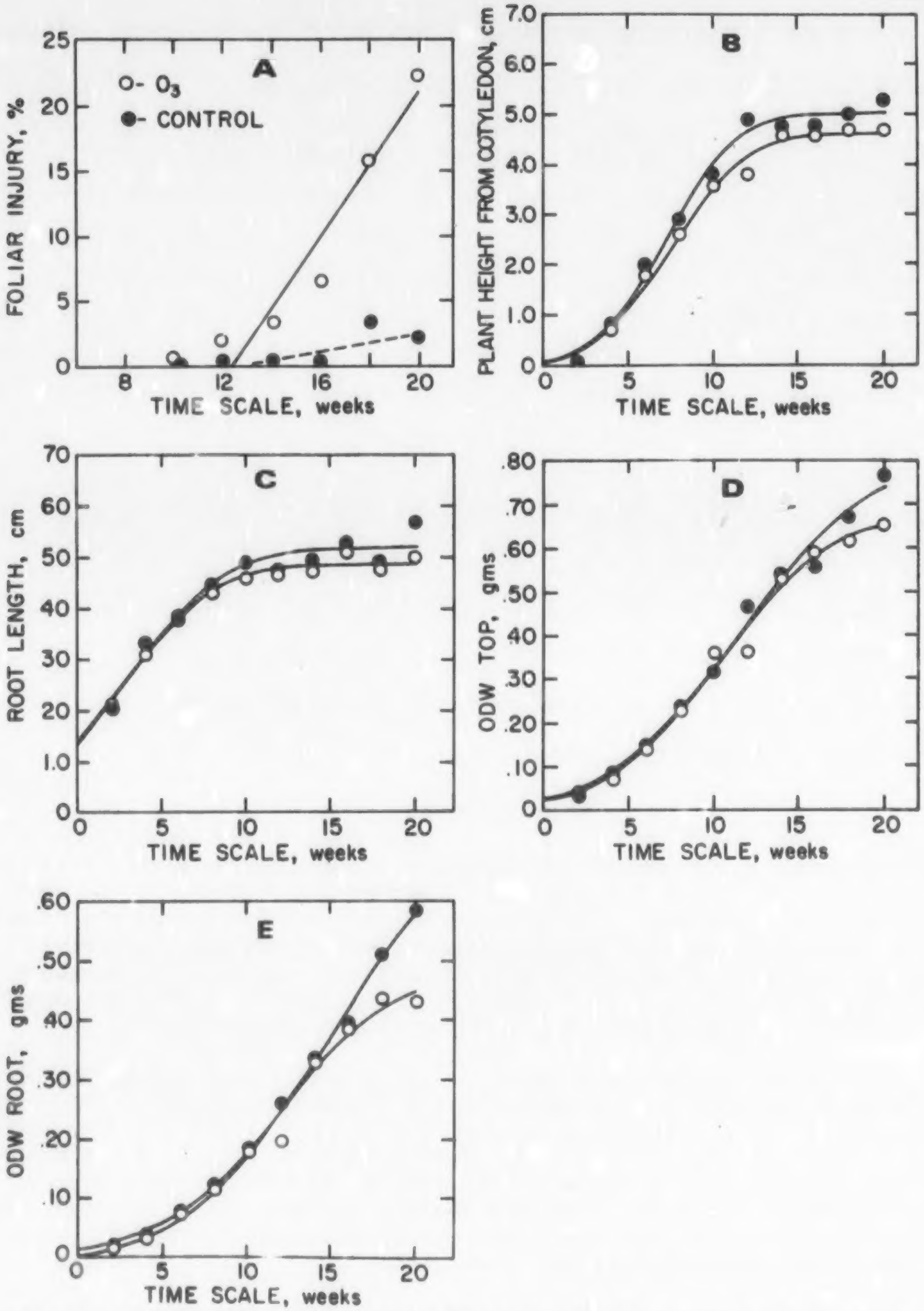

Figure 1 (A to E). Response of Pinus ponderosa Laws. to chronic O_3 exposure: (A) foliar injury, (B) height growth, (C) root growth, (D) top growth (DW), and (E) root growth (DW).

TABLE 2. RESPONSE OF CONIFER SEEDLINGS TO CHRONIC OZONE EXPOSURES

Species	Root length[a]	Plant height[a]	DW foliage[a]	DW stem[a]	DW root[a]	Foliar injury[b]
Douglas fir	7.5	6.1	12.1	14.8	9.4	1
Jeffrey pine	0	2.2	5.6	1.6	5.4	2
Lodgepole pine	13.0	7.7	2.4	8.4	14.7	16
Monterey pine	1.6	0	0	0	0	0
Ponderosa pine	12.1*	11.3	12.4	21.3*	26.3**	20
Shore pine	2.8	2.2	0	6.3	10.1	13
Sugar pine	0	0	0	0	0	0
Western white pine	5.7	0	12.9**	9.1*	12.2	1
Sitka spruce	14.3	0	7.1	13.6	17.9	1

[a] Percent reduction from control

[b] Percent injury on O_3 treatment minus injury on control

* Significant at 90% confidence level

** Significant at 95% confidence level

observations showed significant treatment differences only at a relatively low confidence level (80%). A similar regression analysis for DW root showed that treatment differences were highly significant (98%). Of the growth parameters analyzed, root growth (measured by DW) was most sensitive to the chronic O_3 exposures and differences increased with increased exposure time. The average reduction in root growth from the control at the last observation period (20 weeks of O_3 exposure) was approximately 26%.

The curves for growth of ponderosa pine seedlings by DW top and DW root illustrate that the O_3 treatment affected the growth pattern (Figures 1D and 1E). Growth curves for the O_3 treated plants more closely reached an asymptote than did the corresponding curves for the controls. The O_3 treatment apparently prompted an early growth senescence in ponderosa pine seedlings. The form of the growth curves show that maximum seasonal growth was not reached during the course of this experiment and maximum seasonal growth losses were probably not represented by this experiment.

The direct effects of O_3 on growth of ponderosa pine seedlings observed in this experiment relate to biochemical response of the same test seedlings as reported elsewhere (22). The O_3 exposure increased the Kjeldahl nitrogen and amino acid pools in the roots. The levels of soluble sugars, starch, and phenols tended to increase in the tops (stem + foliage) and decrease in the roots of the O_3-exposed plants. Altered metabolic responses were observed early in the O_3 treatments prior to the appearance of noticeable growth differences. For example, differences in Kjeldahl nitrogen content of the roots of ponderosa pine exposed to O_3 were significantly greater than the controls throughout the experiment; the first observation followed only two weeks of exposure to O_3. In the tops, the starch level in the O_3-treated plants exceeded the control level at all harvests except the first where the amounts were similar. The combined effect of reduced root and shoot growth, stimulation of early senescence, and altered metabolic pools could affect the ability of seedlings to survive harsh environmental elements and reduce competitive ability of O_3-sensitive individuals.

These observations concerning reduced growth and altered metabolic pools in conifer seedlings exposed to low O_3 levels demonstrate the need to consider the response of forest tree vegetation in development and assessment of secondary air quality standards. A great need exists for detailed investigations concerning the physiological and growth response of pollutants on trees and subsequent consequences in surviving harsh environmental elements and competition from associates.

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MACROSCOPIC RESPONSE OF THREE PLANT "SPECIES" TO OZONE, PAN, OR OZONE + PAN

D. D. Davis and R. J. Kohut*

ABSTRACT

Three plant species of varying taxonomic classification were exposed to ozone, peroxyacetyl nitrate (PAN), or a combination of the two pollutants. Species selected were ponderosa pine (Pinus ponderosa var. ponderosa), hybrid poplar (Populus trichocarpa x P. maximowiczii clone 388), and pinto bean (Phaseolus vulgaris "Pinto 111"). Ponderosa pine and hybrid poplar are very susceptible to ozone, but resistant to PAN. Pinto bean is susceptible to both oxidants, responding with two distinctly different and spatially separated symptom types. Exposure of ponderosa pine, while in an ozone-sensitive growth stage, to the combined pollutants resulted in significantly less damage than that induced by ozone alone. In contrast, injury on hybrid poplar induced by combined pollutants was generally greater than that produced by ozone alone. Exposure of pinto bean to combined oxidants completely inhibited the PAN sympton on the abaxial leaf surface and had a synergistic or additive effect on the ozone symptom expression in the adaxial leaf surface.

INTRODUCTION

Air quality standards designed to protect vegetation are often based on research involving the exposure of plants to singular pollutants. However, plants growing in nature are often exposed to ambient air containing multiple pollutants. Two common, phytotoxic photochemical oxidants that may co-exist in polluted air are ozone and peroxyacetyl nitrate (PAN) (10). Although the phytotoxic nature of each oxidant has been clearly established, the response of plants to the combined pollutants has not been reported. Thus, this project was initiated.

The research described herein was conducted over a two-year period from 1974 to 1975. Results from three separate experiments, involving three diverse plant types, have been combined and summarized for publication in this paper.

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HYBRID POPLAR

MATERIALS AND METHODS

Cuttings of hybrid poplar (Populus maximowiczii x trichocarpa), grown out-of-doors in pots, were exposed for four hours in groups of 12 to either 0.18 ppm ozone, 0.18 ppm PAN, or the two pollutants combined at these concentrations. The exposures began when the plants were three weeks old from budbreak and were repeated six times at two week intervals throughout the summer.

Plants were exposed in a specially modified growth chamber (13) at environmental conditions of 23°,75% relative humidity (RH), and 25 Klux light intensity, hereafter described as "standard conditions". Exposure and monitoring techniques for each pollutant were as previously described for ozone (5) and PAN (1, 5, 9, 12). A similar growth chamber housed the control plants at the above environmental conditions. The ozone and PAN monitors (chemiluminescent and electron capture GC, respectively) were pollutant specific and not subject to interference during the combined pollutant exposures. The same exposure and control procedures were also used for poderosa pine and pinto bean.

On the third day after exposure, symptoms were evaluated on the 15 most distal leaves on each plant. The percentage of the leaf surface affected was estimated using previously described reference charts (5). The injury estimates for the 15 leaves on each of the 12 plants were averaged to produce a treatment injury level.

RESULTS

None of the plants exposed to PAN developed visible symptoms. The plants exposed to either ozone or the ozone + PAN mixture developed areas of dark brown to black bifacial necrosis. There was no difference in the time of symptom initiation with either treatment or in the distribution of symptoms on the individual leaves. The recently matured leaves on the plant developed the most severe symptoms in both treatments. Visible symptoms were not observed below the 15 most distal leaves on the plant.

The injury level produced by the ozone + PAN exposure was significantly greater than the sum of that produced by the separate ozone or PAN exposures in four of the six experiments (Table 1); in two experiments the injury levels were not significantly different.

PONDEROSA PINE

MATERIALS AND METHODS

Ponderosa pine seedlings in the juvenile needle stage were raised from seed in pots in the greenhouse until exposure to ozone, PAN, or the combined pollutants. A constant level of 0.05 ppm PAN and 0.40 ppm ozone was maintained in the exposure chamber at standard conditions. On two consecutive days, 120 pine seedlings were exposed to this combined dosage for 2, 4, 6, or 8 hours beginning at 0900 hours. Following exposure, plants remained in growth chambers for five days at standard conditions during symptom development.

TABLE 1. VISUAL ESTIMATES OF THE PERCENTAGE OF ADAXIAL INJURY PRODUCED ON HYBRID POPLAR BY EXPOSURE FOR 4 HOURS TO EITHER 0.18 ppm OZONE, 0.18 ppm PAN OR THE TWO POLLUTANTS COMBINED AT THESE CONCENTRATIONS.

Exposure Dates (1975)	% Injury [a]			Confidence level of the synergistic interaction (F-test)
	Ozone	PAN	Ozone + PAN	
June 20-22	0.8	0.0	3.7	95%
July 5-7	0.0	0.0	0.6	N.S.[b]
July 19-21	0.4	0.0	2.1	90%
Aug. 3-5	5.4	0.0	5.8	N.S.[b]
Aug. 16-18	28.8	0.0	52.6	99%
Aug. 29-31	0.0	0.0	2.8	99%

[a] The mean percentage of foliar injury on the 12 plants in the treatment.

[b] No significant pollutant interaction at the 90% confidence level.

RESULTS

The symptoms induced by ozone or ozone + PAN were identical and were similar to typical ozone injury on ponderosa pine. Seedlings were tolerant of PAN and did not develop symptoms. The percentage injury induced by ozone + PAN at 4, 6, and 8 hours was significantly (0.01) less (antagonistic response) than that produced by ozone alone (Figure 1). Injuries from the two-hour exposures were statistically (0.05) similar.

PINTO BEAN

MATERIALS AND METHODS

Ten-day old pinto bean plants in the trifoliate leaf stage were exposed for four hours to either 0.30 ppm ozone, 0.05 ppm PAN, or the two combined at these concentrations. Twenty plants maintained in growth chambers were used in each exposure. A series of three exposures was conducted on three consecutive days and replicated five times. Control plants were maintained in another chamber at the same environmental conditions during the exposure. After the exposure, all plants were returned to their original growth chambers during symptom development.

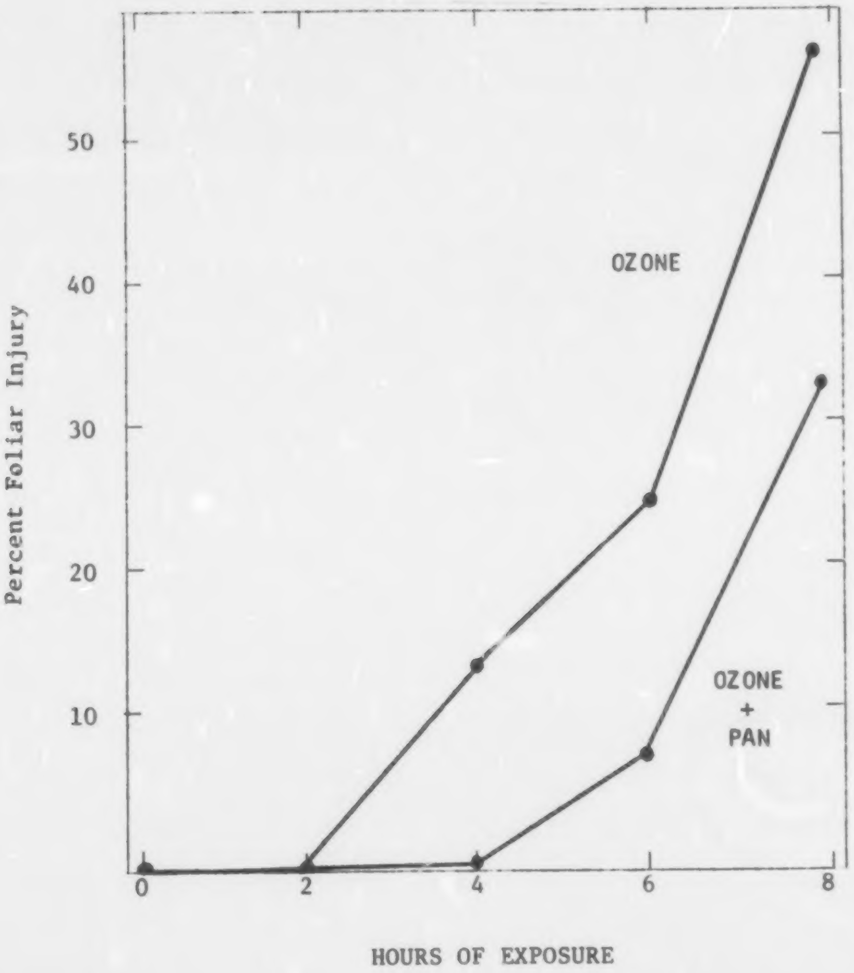

Figure 1. Percent foliar injury on primary needles of ponderosa pine exposed to 0.40 ppm ozone, or 0.40 ppm ozone + 0.05 ppm PAN for 2,4,6 or 8 hrs. Each dot represents the average value determined for 30 seedlings in two replications. PAN alone induced no injury. Ozone alone induced significantly (.01) greater foliar injury than did ozone + PAN at the 4,6, and 8 hour exposures (T-test). Injury was not induced by two hours of exposure.

The first trifoliate leaf on each plant was evaluated for injury three days after exposure. The adaxial and abaxial surfaces of leaflets were evaluated separately. The symptom types and the percentage of the leaflet surface affected by each type were recorded using the two factor system previously described (5). An average percent plant injury and treatment injury was calculated for each leaf surface. Percent adaxial and abaxial injury were also averaged to calculate injury on the combined leaf surface.

RESULTS

The ozone exposures produced a typical light tan fleck on the adaxial leaf surface, while PAN produced primarily abaxial bronzing with some light tan bifacial necrosis. The symptoms produced by the combined pollutant exposures were mainly restricted to the adaxial leaf surface with a nearly complete suppression of symptoms on the abaxial surface. The adaxial symptom produced by the combined pollutants was fleck similar in appearance to that produced by ozone but slightly more yellow. In the one replication where abaxial symptoms were produced in response to the combined pollutant exposure, the symptom was a bronzing similar to that produced by PAN.

Three of five replications indicated a synergistic response on the adaxial surface in the combined pollutant exposures, while the response was additive in the other two replications (Table 2). Injury on the abaxial leaf surface indicated an antagonistic response in all five replications. When the combined leaf surface response was evaluated, all of the replications indicated an antagonistic response.

DISCUSSION

The possibility that ozone and PAN might interact chemically in the exposure chamber atmosphere was investigated to ensure that the observed interactions were not the result of chemical reactions within the chamber. A stable ozone concentration was established in the exposure chamber and PAN was then introduced. The chemiluminescent monitor provided a continuous reading of ozone concentration and indicated that PAN had no effect on the ozone concentration. The procedure was then reversed by establishing a stable PAN concentration and introducing ozone. No change in PAN concentration was detected using the electron capture GC. Therefore, it was possible to discount an atmospheric reaction between the two pollutants as an explanation for any changes in injury levels produced by the combined pollutants. This indicated that the diverse response of the three taxonomically different species was physiological in nature within the host. The results of these exposures provide the first evidence that the photochemical oxidants ozone and PAN can interact when producing injury to vegetation.

The symptom types induced by the combined pollutants was typical of that induced by ozone alone. The foliage of hybrid poplar produced brown to black areas of bifacial necrosis, typical of ozone injury on this clone (5). The needles of ponderosa pine showed a chlorotic mottle, similar to that induced by ozone alone (3,7,8). This was as expected, since these two species were resistant to PAN (2,5), as are many woody plants (4). However, pinto bean, which is sensitive to PAN, also responded with an adaxial fleck similar in appearance to that caused by ozone alone. Thus, in each case the combination of ozone and PAN induced symptoms on all three species similar to those induced by ozone. This is somewhat analagous to the symptom response of various species to mixtures of ozone and sulfur dioxide, in which the ozone type symptom was augmented (6,11). The recently matured foliage of a plant is generally recognized as being most sensitive to ozone. The symptoms observed in both the ozone and ozone/PAN treatments were most severe on this recently matured tissue with all three plant types.

TABLE 2. PERCENTAGE VISIBLE FOLIAR INNURY ON THE PRIMARY LEAVES OF PINTO BEAN PRODUCED BY 4-HOUR EXPOSURES TO EITHER 0.30 ppm OZONE, 0.05 ppm PAN, OR THE TWO POLLUTANTS COMBINED AT THESE CONCENTRATIONS.

Rep.	Leaf Surface	% Injury[a]			Response[b]
		Ozone	PAN	Ozone/PAN	
1	Adaxial	20	4	25	NS
	Adaxial	0	66	0	ANT
	Combined	10	35	13	ANT
2	Adaxial	12	13	24	NS
	Adaxial	0	57	4	ANT
	Combined	6	35	14	ANT
3	Adaxial	25	3	42	SYN
	Adaxial	0	35	0	ANT
	Combined	12	18	21	ANT
4	Adaxial	21	5	45	SYN
	Adaxial	0	53	0	ANT
	Combined	10	29	22	ANT
5	Adaxial	28	4	45	SYN
	Adaxial	0	23	0	ANT
	Combined	14	13	22	ANT

[a] The mean percentage of visible foliar injury for the 20 plants in each treatment.

[b] Response was evaluated for each leaf surface

NS = non-significant at 95% level of confidence;
ANT = antagonistic response;
SYN = synergistic response (F-test)

These results indicate that a plant does not have to be susceptible to both pollutants for them to interact and produce injury. Such findings should be considered when evaluating the importance of an air pollutant in the field. It must be remembered that in addition to the pollutant of interest, a plant in the field may also be subjected to other pollutants. While these pollutants may be considered innocuous on their own, their potential to enter into interactions must be considered. Also, plant response to simultaneous exposure to ozone and PAN will likely vary, depending upon the species, dosage and ratio of the combined pollutants, age of plant or leaf, leaf surface, environmental conditions, and method of evaluation. This makes it very difficult to consider results from interaction studies when formulating air quality standards, unless constant findings are achieved over a wide range of species and conditions.

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RELATIVE SENSITIVITY OF EIGHTEEN HYBRID COMBINATIONS OF PINUS TAEDA L. TO OZONE

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ABSTRACT

Loblolly pine seedlings were exposed to ozone (O_3) to select a sensitive and a tolerant cross to be used as bioindicators of ambient air pollution levels. Eighteen hybrid combinations of loblolly pine were screened for sensitivity to 0.10-0.25 μliter ozone/liter air. Cross 6-13 x 2-8, the most sensitive in five of eight exposures, was among the five most sensitive in seven of eight exposures. In both replications of 0.15 μliter O_3/liter air 6-13 x 2-8 was significantly more sensitive than the remaining 17 crosses. In two replications of 0.25 μliter O_3/liter air 6-13 x 2-8 was significantly more sensitive than 14 and 13 of the remaining 17 crosses. Little injury was noted on the crosses exposed to 0.10 μliter O_3/liter air, and it was in one of those replications that 6-13 x 2-8 was not among the five most sensitive. Cross 6-13 x 2-8 was never among the ten most tolerant. Cross 540 x 504 was among the six most tolerant in six of eight exposures. Three crosses were among the six most tolerant lines in the majority of the eight exposures and had no injury in two of those eight exposures. The results indicated that it was feasible to use sensitive and tolerant crosses of loblolly pine as bioindicators of ambient pollution levels. The results also indicated that sensitivity to O_3 may be heritable enough to warrant further study into the feasibility of breeding programs.

INTRODUCTION

The deleterious effects of air pollution on plant life have been known for many years; however, increasing human populations, increased mobility of our society, and increased demand for power have served to intensify the problem. Recently, relatively high levels of ozone have been monitored in remote areas of southwestern Virginia (3). High sulfur dioxide and oxides of nitrogen levels of short duration have also been monitored at Blacksburg, Virginia.

A periodic industrial source of air pollutants, the Radford Army Ammunition Plant (RAAP), is located in southwest Virginia. This industrial complex is located in a forested geographic bowl, which allows the build up of three major pollutants: ozone (O_3), sulfur dioxide (SO_2), and oxides of nitrogen (NO_x).

The RAAP began operation in 1939 and has had three peaks in production corresponding with the national defense efforts of the United States. The production rate at this installation was used to estimate the amount of air pollution emitted.

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Past studies at the RAAP have demonstrated significant negative correlations between cyclic industrial production levels and the annual radial increment growth of planted loblolly pines (5); other studies reported similar data with several other forest species (4, 6). Research elsewhere has demonstrated that loblolly pine was relatively sensitive to O_3 or SO_2 (1, 2). The current investigators felt that loblolly pine would therefore be a good candidate for use as a bioindicator of the reduced RAAP air emissions as abatement facilities become operational.

Loblolly pine is the most important species to the forest industry in the South. The Commonwealth of Virginia planted 83 million loblolly pine seedlings in 1973, and the Southern Forest Tree Improvement Program has an active breeding program based on gaining a 5% improvement in tree growth form, growth rate, fiber content, disease resistance, and several other important parameters. The importance of the species generated the breeding program from which we have been able to obtain seed of controlled crosses of loblolly pine. Controlled crosses minimize variation in the plant population much the same, although not as effectively, as clonal selection.

Part of a continuing research program to biologically monitor ambient air pollution levels has involved the use of a tolerant and a sensitive line of loblolly pine planted in open-top chambers. Eight trees of each line have been planted within chambers drawing ambient air or charcoal-filtered air; an open plot was also established. Height growth, needle length, and foliar symptoms on these trees are to be measured over the next three to six years.

The objective of the study reported within this paper was to screen several hybrid crosses of loblolly pine for sensitivity to O_3 and to choose the most sensitive and most tolerant cross for use in the field studies utilizing open-top chambers. A secondary objective was to collect preliminary data as to whether or not breeding for tolerance or sensitivity of loblolly pine to air pollution would be feasible.

MATERIALS AND METHODS

Seed of 18 hybrid lines of loblolly pine was obtained from the Southern Forest Tree Improvement Program and was greenhouse grown in a 2:2:1 weblite: vermiculite:peat moss soil mix in four-inch plastic pots with four trees per pot. Each pot received 1 gram of osmocote fertilizer and was watered routinely. The greenhouse was provided with charcoal-filtered air and supplemental lighting of 21,000 lux was provided on a 14-hour photoperiod by high pressure sodium lamps.

During July 1975 when the trees were 2 1/2 to 4 weeks old, they were exposed to ozone for eight hours at corrected Mast readings of 0.10, 0.15, 0.20, and 0.25 μliter/liter air (10, 15, 20, and 25 pphm). The exposure chambers employed a one-pass-through air system, drawing in charcoal-filtered air having a chamber residence time of two minutes. The pollutants were injected into the intake lines just prior to their entry into each chamber. Pollutant concentrations were maintained at the desired levels by monitoring at plant height and adjusting the flow of pollutant into the chamber. The O_3 levels were monitored continuously with Mast oxidant meters and spot checked regularly with the 1% neutral buffered potassium iodide (KI) method. Lighting for the chambers was 30,000 lux provided by high-pressure sodium lamps. Environmental conditions were 25-30°C and 70-85% RH.

Foliar symptoms were evaluated prior to exposure, immediately following exposure, and 1, 7, 14, and 21 days following exposure. Symptom expression was assigned values of 1-7 in an attempt to place an importance on each symptom type (Table 1).

TABLE 1. SYMPTOM CLASSES USED TO EVALUATE LOBLOLLY PINE HYBRIDS EXPOSED TO VARIOUS LEVELS OF O_3 FOR 8 HOURS

SYMPTOM CATEGORIES	
1	Mottle
2	Chlorotic spot
3	Chlorotic band
4	Chlorotic tip
5	Necrotic spot
6	Necrotic band
7	Necrotic tip

The severity value was then multiplied by the percent of the needle affected. This yielded a severity index for each needle. The severity indices were summed for all needles on a tree to yield a T (total injury) value. The T value was then divided by the total number of injured needles to yield an I (average injured needle) value; an indication of how severely each needle was injured. The T value was also divided by the total number of needles on the tree to yield an A (average of all needles) value; an indication of how severely each tree was injured. To provide smaller numbers to work with statistically, a value of .5 was added (to eliminate 0 values) to each of the T, I, and A values, and then the square root of each value was calculated. Each of the respective values was then summed and averaged for the four trees of each cross. This procedure yielded six values (T, St, I, SI, A, SA) denoting the same severity index for each cross. An ANOVA was calculated using each value, and the means for each cross were tested by Duncan's Multiple Range Test.

RESULTS

There was substantial variation in the symptom expression response to O_3 between the loblolly pine crosses tested. There also was substantial variation in the symptom expression of the individual trees within a given cross. In ranking the means, however, in terms of sensitivity and tolerance to O_3 there was virtually no difference between the six (T, ST, I, SI, A, SA) severity index values, and therefore the ST value was chosen to work with for the rest of the analyses.

The mean symptom severity indices for cross 6-13 x 2-8 in replication 1 of 15 pphm O_3/8 hours have been listed in Table 2.

TABLE 2. SYMPTOM SEVERITY INDICES OF SENSITIVE LOBLOLLY PINE CROSS 6-13 x 2-8 EXPOSED TO 15 PPHM O_3 FOR EIGHT HOURS FOR USE IN TREE BIOINDICATOR SYSTEMS AT RAAP

INJURY INDICES*	
T - 6114	ST - 74
I - 306	SI - 17
A - 175	SA - 12

*All indices are an average of four values; T is the average total injury value, I is the average of total value divided by the number of injured needles, and A is the average of total value divided by the total number of needles. The ST, SI, and SA values are, in effect, the square roots (before averaging) of T,I, and A values.

The variation between the four individual values that were averaged to yield the T, I, and A values accounted for their respective square root values (which were taken before averaging) not being exact square roots.

For example, with no variation between the four values that make up the T value in Table 2, the ST value would be the square root of the T value.

The symptom progression of four of the crosses following exposure to 15 pphm O_3/8 hours have been listed in Table 3.

Lines 6-13 x 2-8 and 2-40 x 2-8 were the two most sensitive and 540 x 504 and 501 x 504 were the two most tolerant. There were no symptoms immediately following the exposure, but symptoms developed very rapidly on the most sensitive line. If all the needles were 100% necrotic, the injury index would have been approximately 150. A value of 74 indicated relatively severe injury; all needles 50% necrotic, half of the needles 100% necrotic and the rest asymptomatic, or somewhere in between.

Table 4 shows the two most sensitive loblolly pine crosses and the number of other crosses that each of these two lines was more sensitive than to O_3 (two replications each of 25 and 15 pphm O_3/8 hours). In both replications of 15 pphm O_3/8 hours, cross 6-13 x 2-8 was significantly more sensi-

TABLE 3. SYMPTOM EXPRESSION (ST SEVERITY INDEX VALUE) OF FOUR LOBLOLLY PINE CROSSES EXPOSED TO 15 PPHM O_3 FOR 8 HOURS IN THE DEVELOPMENT OF A TREE BIOINDICATOR SYSTEM AT THE RAAP

	DAYS AFTER EXPOSURE			
	1	7	14	21
6-13 x 2-8*	58	66	71	74
2-40 x 2-8	2	9	13	14
540 x 504	0	0	3	4
501 x 504	0	0	0	0

*Crosses 6-13 x 2-8 and 2-40 x 2-8 were relatively sensitive and crosses 540 x 504 and 501 x 504 were relatively tolerant.

TABLE 4. THE TWO MOST SENSITIVE LOBLOLLY PINE CROSSES AND THE NUMBER OF CROSSES THAT EACH WAS SIGNIFICANTLY MORE SENSITIVE TO O_3 THAN IN THE DEVELOPMENT OF A TREE BIOINDICATOR SYSTEM AT THE RAAP

	TREATMENTS*			
	25 pphm/8 hr		15 pphm/8 hr	
Cross	1	2	1	2
6-13 x 2-8	14	13	17	17
2-40 x 2-8	7	11	0	0

*Two replications each of 25 pphm O_3/8 hours and 15 pphm O_3/8 hours.

tive than all of the remaining 17 crosses. At 25 pphm/8 hours, cross 2-40 x 2-8 was significantly more sensitive than 7 and 11 of the remaining 17 lines.

The symptom severity indices of the two most and two least sensitive crosses over two replications each of the four ozone levels have been listed in Table 5. Any value underlined denotes it was ranked among the five most sensitive crosses. A value with a line over it signifies the cross was among the six most tolerant.

Cross 6-13 x 2-8, the most sensitive in 5 of 8 of the exposures, was among the five most sensitive in 7 of 8 of the exposures. It was also significantly more sensitive than all remaining crosses in both replications of 15 pphm O_3 for eight hours. Cross 540 x 504 was among the six most tolerant in 6 of 8 of the exposures, and in the one exposure in which it was not it sustained little injury. Cross 501 x 504 was among the six most tolerant in 7 of 8 exposures, but in the remaining exposure, it was among the five most sensitive.

Table 6 shows the effect of time of year on the sensitivity of loblolly

TABLE 5. SUMMARY OF DATA USED IN SELECTION OF 6-13 x 2-8 AND 540 x 504 FOR USE AS BIOINDICATOR LINES IN FURTHER STUDIES AT THE RAAP

	OZONE TREATMENT							
	25 pphm/8 hr Rep		15 pphm/8 hr Rep		20 pphm/8 hr Rep		10 pphm/8 hr Rep	
Cross	1	2	1	2	1	2	1	2
6-13 x 2-8	$\underline{90}$*	$\underline{105}$	$\underline{74}$	$\underline{97}$	$\underline{18}$	$\underline{5}$	$\underline{3}$	1
2-40 x 2-8	$\underline{76}$	$\underline{99}$	$\underline{14}$	$\underline{9}$	$\underline{23}$	$\underline{9}$	$\overline{0}$	1
540 x 504	40	$\overline{30}$	4	$\overline{2}$	$\overline{3}$	$\overline{1}$	0	$\overline{1}$
501 x 504	$\overline{8}$	$\overline{5}$	$\overline{2}$	$\underline{17}$	$\overline{10}$	$\overline{0}$	$\overline{0}$	$\overline{0}$
Highest value+	90	105	74	97	39	16	3	2

bar under - ranked among five most sensitive of eighteen
bar over - ranked among six most tolerant of eighteen

* - Symptom severity of the two most and two least sensitive loblolly pine crosses in two replications each of four levels of ozone.

+ - The highest value of any cross for each replication is listed at the bottom.

TABLE 6. SYMPTOM SEVERITY INDEX (T VALUE) OF THE MOST SEVERELY INJURED LOBLOLLY PINE CROSS OVER A VARIETY OF EXPOSURE CONDITIONS AT DIFFERENT TIMES OF THE YEAR. TREE AGE WAS HELD RELATIVELY CONSTANT FOR EACH EXPOSURE

Exposure Date	pphm O_3/hr	Severity Index
4/22	50/8	1191
5/5	25/8	163
6/9	25/8	40
7/2	15/8	6114
7/8	15/8	9935
7/14	20/8	1734
7/22	20/8	450

pine to ozone.

The injury (T) values increased from 163 and 40 in May and June to 6114 and 9935 in the first week of July, and lower O_3 concentrations were used in the latter exposures. Then in the middle of July, the values drop again to 1734 and 450. Tree age at time of exposure was held relatively constant.

DISCUSSION

The preceding data, along with preliminary NO_2 and SO_2 screening data, indicate that it is feasible to use sensitive and tolerant crosses of loblolly pine as bioindicators of pollution abatement programs at the RAAP. Based on foliar symptoms in response to O_3, there is a good breakdown between the most sensitive and the most tolerant crosses. Preliminary screening indicates that those lines most sensitive to O_3 are also the most sensitive to NO_2 or SO_2.

Crosses 6-13 x 2-8 and 540 x 504 were selected for use as the bioindicators to be used in the open-top chamber field studies at the RAAP. Cross 6-13 x 2-8 was significantly more sensitive than 540 x 504 in five of the eight replications. In the remaining three, neither cross sustained significant injury. The difference between the crosses was based solely on foliar symptoms. A goal of the open-top chamber study will be to demonstrate effects on growth as well as foliar symptoms.

The results indicate that sensitivity to O_3 may be heritable enough to warrant further study into the feasibility of breeding programs. Besides the 18 crosses included in this data, a limited number of seedlings of four other crosses were also screened. One of these four (2-8 x 523) was also a very sensitive cross, demonstrating that the three most sensitive crosses all involved line 2-8. Information on how the primary needles of each tree responded is now recorded, and information on how the secondary needles respond will be accumulated in future studies. The responses must remain consistent for breeding programs to be feasible, and for the different crosses to be useful as bioindicators to be planted at the RAAP to demonstrate the success or failure of the abatement programs.

The time of year effect was an interesting but puzzling problem. It has been noted by several other researchers on several other species of plants. Peak sensitivity, holding age constant, usually occurred at the end of June and the first part of July. It may be tied partly to age, day length, and RH in a field situation, but even controlling those variables the difference still occurred. The dramatic difference noted in this study may be due in large part to RH. During the winter and spring months it was difficult to maintain high RH levels in the exposure chambers. This effect may be very significant at the RAAP. At times when plants were not in a sensitive condition, the pollutant levels could possibly be higher without causing significant adverse effects to the plants. This data also demonstrates that we need the results of combined pollutant, long-term ambient studies to be able to evaluate more fully the growth impact of the pollution regime.

CONCLUSIONS AND RECOMMENDATIONS

Based on foliar symptoms, there appeared to be enough variation among lines of loblolly pine to allow their use as bioindicators of ambient air pollution. The results also indicated that sensitivity or tolerance may be heritable enough to warrant further study into the feasibility of breeding programs.

Future study must examine the effects on loblolly pine of O_3, NO_x, and SO_2 singly and in combination. Preliminary data indicates that those lines sensitive to O_3 are also sensitive to NO_2 or SO_2. Growth impact due to long-term low-level exposures to combinations of all three pollutants must also be examined in field studies and in controlled environment studies.

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EFFECTS OF OZONE AND SULFUR DIOXIDE SINGLY AND IN COMBINATION ON YIELD, QUALITY, AND N-FIXATION OF ALFALFA

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ABSTRACT

Field exposures of alfalfa, Medicago sativa L. cv. Mesa-Sirsa to ozone (O_3) (100 and 200 $\mu g/m^3$) and sulfur dioxide (SO_2) (156 $\mu g/m^3$) were conducted during two growing seasons to determine growth, quality, and yield effects. Two experiments were conducted. In the first, O_3 was administered six hours per day, seven days per week to established alfalfa plants grown in peat-vermiculite. The second experiment involved sand-grown alfalfa plants with O_3 (seven hours per day) and sulfur dioxide (24 hours per day) applied singly and in combination with O_3, seven days per week.

All studies were conducted at the U.S. Environmental Protection Agency's (EPA) Corvallis Environmental Research Laboratory farm site in Corvallis, Oregon. Parameters measured included dry weight (DW) of forage, stubble, and roots; total protein, amino acids, total nonstructural carbohydrates (TNC), phenols, and β-carotene contents; and nitrogen-fixing capacity. Plants were routinely harvested when controls reached 1/10 bloom. Root and stubble data were obtained only at the second harvest of the sand alfalfa study.

Forage dry weight of established plants was 50 percent of control at the third harvest following 70 days of exposure to 200 $\mu g/m^3$ (.10 ppm) O_3. After 68 days exposure to 100 $\mu g/m^3$ (.05 ppm) O_3, 156 $\mu g/m^3$ (.06 ppm) SO_2, or the mixture, forage stubble and root dry weights were 50 to 60 percent of control at the second harvest for alfalfa grown in sand (plus Hoagland's nutrient solution minus nitrogen). In both studies, dry weights of all pollutant treatments (compared to controls) showed a greater reduction with successive harvests. In both studies, the protein content per unit weight of plant forage was increased in the pollutant-stressed plants by the last harvest. The net effect of the pollutants, however, was a reduction in total protein produced per treatment resulting from reduced production of total dry matter. The O_3 treatment (200 $\mu g/m^3$) also increased the amino acids content in established alfalfa at the last harvest. However, due to reduced dry matter production, the total amino acid produced per sample was reduced. Ozone decreased β-carotene content on both a unit weight and total weight basis at the last harvest of established alfalfa. The total TNC in forage, stubble, and roots of the pollutant treatments was reduced by approximately 50 percent at the last harvest in both studies. The O_3, SO_2 or O_3 + SO_2 sand alfalfa treatments caused approximately a 40 to 60 percent decrease in total symbiotically fixed-nitrogen (N) in the forage, stubble, and roots at the last har-

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vest. The effects of the O_3 and SO_2 mixture on alfalfa did not differ greatly from the effects of the single pollutants.

INTRODUCTION

Alfalfa, Medicago sativa L., a perennial legume, is widely grown throughout the world, with approximately 11 million hectares grown in the United States. It has been called "Queen of Forage Crops" because of the superior protein, mineral and vitamin content, yield and total feed value.

The following effects of ozone (O_3) on alfalfa have been reported: Howell et al. (1) noted variations in the visible injury on 14 strains exposed four hours to 400 $\mu g/m^3$ O_3 in the greenhouse; Tingey and Reinert (2) found 12 and 22 percent reductions in forage (stems and leaves) and root dry weights, respectively, after greenhouse exposure to 98 $\mu g/m^3$ O_3 for 40 hr/week from seedling to harvest. Oshima (3) reported that a dose (concentration x time) of 2500 pphm hours greater than 10 pphm (200 $\mu g/m^3$) O_3 was required for significant yield reductions to occur in Moapa 69 alfalfa grown in the ambient air.

Changes in alfalfa growth and metabolite pools resulting from O_3 exposures are important because they affect crop quality and yield. They also may (a) reflect pollution-induced changes in plant metabolism, (b) affect plant resistance to stress, and (c) affect plant regrowth after winter dormancy or cutting. Other studies conducted to determine changes in metabolite pools in plants exposed to O_3 have focused on high concentration, short duration exposures (4, 5, 6). Little data on long-term, chronic O_3 effects are available. Ponderosa pine seedlings exposed to 200 $\mu g/m^3$ O_3 for 20 weeks showed a retention of sugars and starch in the top of the plant and a reduction in the roots (7).

Metabolites from the stems and leaves of legumes are translocated to the roots to provide the energy needed to reduce and incorporate atmospheric nitrogen (N) into the organic forms that can be used for growth (8). This suggests that a reduction in metabolites translocated to the alfalfa roots reduces the amount of atmospheric nitrogen (N) fixed, thus reducing plant growth and yield.

The objective of this research was to determine the effects of chronic levels of O_3 and sulfur dioxide (SO_2) (singly and in combination) on alfalfa yield, quality and N-fixation as they related to changes in metabolite levels.

EXPERIMENTAL PROCEDURES

Two experiments were conducted with alfalfa, Medicago sativa L. cv. Mesa-Sirsa at the EPA's Corvallis Environmental Research Laboratory Farm in Oregon. In each study, seed was inoculated with an N-fixing bacteria before planting in 20 cm diameter plastic pots. For the established study, the pots were filled with a peat-vermiculite mix (Jiffy Mix-Plus) containing a slow release fertilizer; for the sand study, 20 mesh silica sand with a modified Hoagland solution minus N was added daily. The only nitrogen source available to the plants in the sand experiment was symbiotically fixed atmospheric N.

Two plants were grown in each of the pots allocated per treatment in the established (18 pots) and sand (10 pots) alfalfa studies. Established plants were obtained by withholding the alfalfa from pollutant treatment until after the first harvest. Treatment of plants in the sand study began when they were approximately 10 cm seedlings.

In the established study, plants were exposed for 70 days to either charcoal-filtered air (control), or 200 μg/m^3 O_3 in charcoal-filtered air; each treatment was replicated three times. Ozone was added six hours per day (9 a.m. to 3 p.m.), seven days per week as described by Heagle et al. (9). All plants received charcoal-filtered air without ozone the remaining 18 hours each day.

Plants were exposed for 68 days in the sand alfalfa study. One exposure chamber was allocated to each treatment: (a) charcoal-filtered air (control), (b) 100 μg/m^3 O_3, (c) 156 μg/m^3 SO_2, and (d) 100 μg/m^3 O_3 plus 156 μg/m^3 SO_2. Ozone was added seven hours per day (9 a.m. to 4 p.m.), seven days per week in charcoal-filtered air; sulfur dioxide was added to either charcoal-filtered air or charcoal-filtered air plus ozone 24 hours per day, seven days per week as described by Heagle et al. (10). These plants also received charcoal-filtered air when the pollutants were not present. The tops (forage) of all plants were clipped 8 cm above the growing medium surface when the controls reached the 1/10 bloom stage of growth. Dry weight (DW) of forage was obtained at each harvest in both studies by drying all plant material from each pot at 70°C. for 48 hours. Root and stubble dry weights were obtained only at the last harvest (second) of the sand alfalfa experiment.

Forage from two pots were batched in the established alfalfa before metabolite analysis, providing 9 samples per treatment compared to 10 in the sand alfalfa study. Dried plant material was analyzed for total protein, amino acids, phenols, total nonstructural carbohydrates (TNC) and β-carotene content by methods previously described (7, 11, 12).

The data are presented as percent of control with associated 95 percent confidence limit estimates or other indicated levels for statistically significant differences.

RESULTS

ESTABLISHED ALFALFA EXPERIMENT

Forage metabolite content per unit weight of sample at the first harvest did not significantly vary from the control for any of the metabolites measured (Figure 1). At the second harvest, the amino acid and phenol content of the forage was significantly higher in the O_3-treated plants; no significant differences occurred in the other metabolites. By the third harvest, amino acid and total protein content were 119 and 128 percent of the control, respectively. There were no significant differences from the control in total nonstructural carbohydrates (TNC), total phenols or lignin contents, but the β-carotene content was reduced to 76 percent of control.

At the first harvest, the total amount of measured metabolites produced

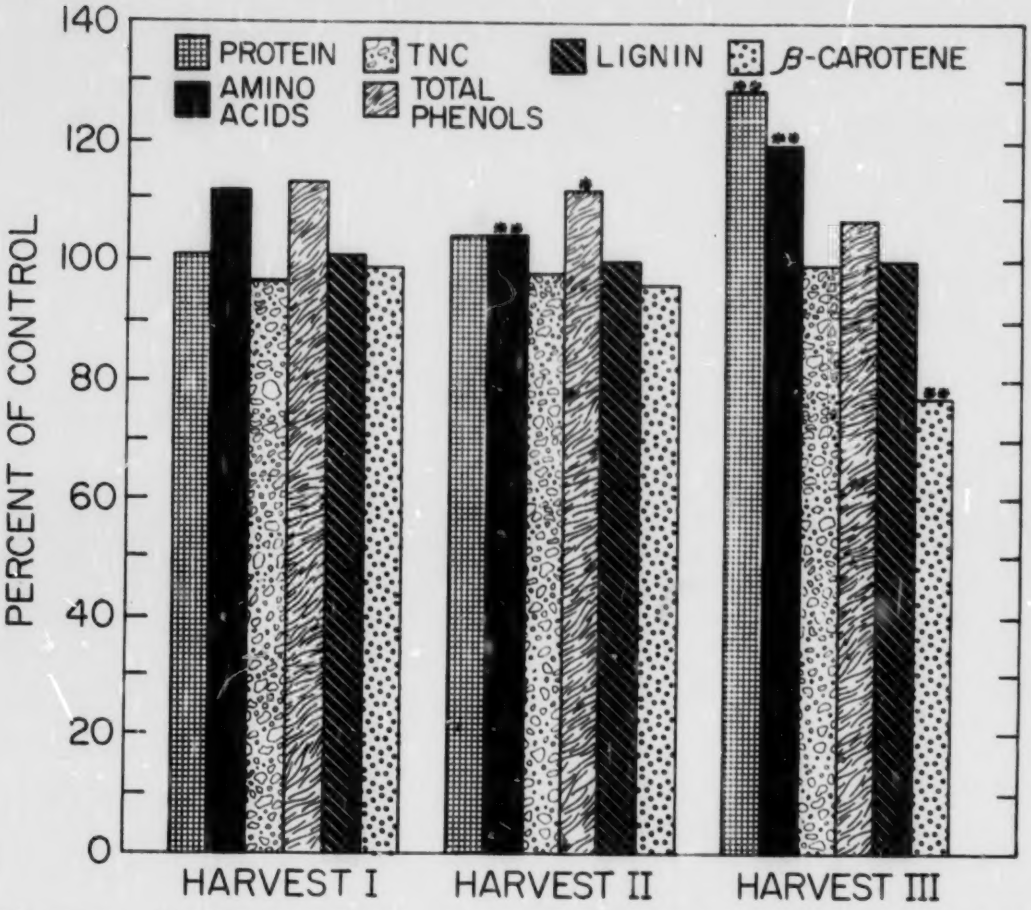

Figure 1. Metabolite content of established alfalfa forage (unit weight). *Each value is based on nine observations for each mean. Significant differences are shown as: *5% and **1%.

per sample in forage by O_3-exposed plants did not vary significantly from the control (Figure 2). The only significant differences occurring at the second harvest were a reduction (75% of control) in TNC and dry weight (80% of control) produced per sample of forage stressed with O_3. By the third harvest, the total metabolites produced per sample of O_3-stressed plants were 40 to 60 percent of control for each of the metabolites investigated. The dry weight of forage treated with O_3 was 49 percent of control at the third harvest.

SAND ALFALFA EXPERIMENT

At first harvest, TNC forage content on a unit weight basis in plants treated with O_3 or SO_2 singly was greater than the control (Figure 3); this significant difference was not present at the second harvest. However, root or stubble TNC content on a unit basis was 80 to 85 percent of control for each of three pollutant treatments at the second harvest. The protein content of the forage on a unit weight basis at first harvest was not significantly different from the control in any of three treatments (Figure 4). By

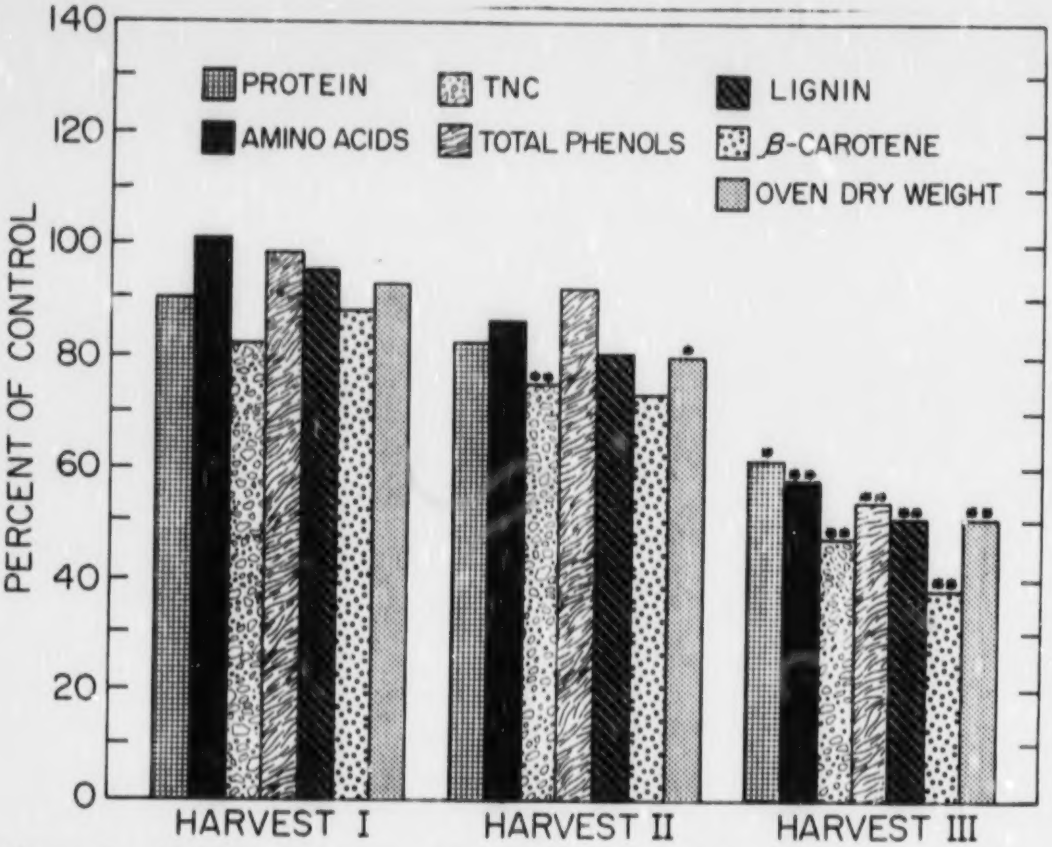

Figure 2. Metabolite content of established alfalfa forage (total weight).

*The metabolite content per unit weight was multiplied by the total treatment weight to give total metabolite produced. Each percent is based on nine observations for each mean. Significant differences are shown as: *5% and **1%.

the second harvest, protein content in the forage was 113, 123, and 123 percent of control for the O_3, SO_2, and $O_3 + SO_2$ treatments, respectively. However, the protein content of the stubble or roots at the second harvest was not significantly different from the control regardless of treatment. At the first harvest, the total amount of TNC produced per treatment in forage of plants exposed to O_3, SO_2, and $O_3 + SO_2$ was 68, 57, and 62 percent of control, respectively (Figure 5). By the second harvest, the total amount of TNC in the forage per sample was further reduced to 45, 47, and 54 percent of control, respectively. Totals for root TNC were approximately 43 percent of control for each of the pollutant treatments.

The total amount of protein present in forage at the first harvest was approximately 63 percent of control in both the SO_2 and $SO_2 + O_3$ treatments; the total protein in the O_3 treatment was not significantly different from the control (Figure 6). At the second harvest, the total protein produced in forage of plants exposed to O_3, SO_2, and $O_3 + SO_2$ was 58, 62, and 69 percent

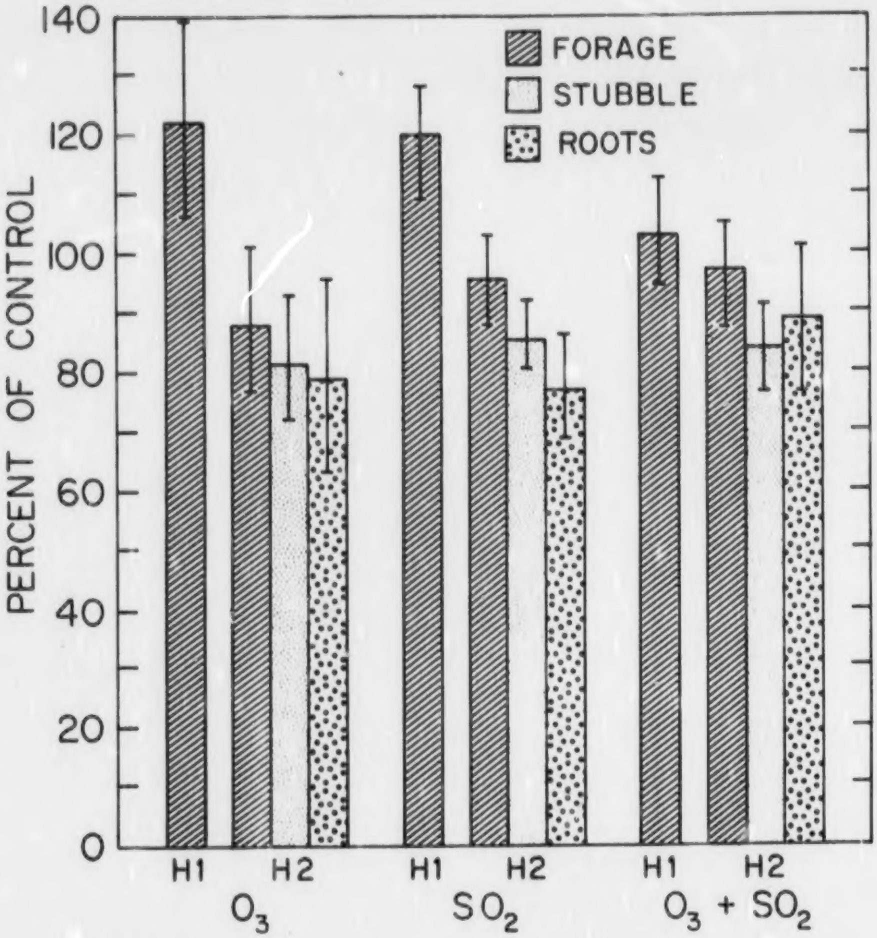

Figure 3. Total nonstructural carbohydrate content of sand alfalfa (unit weight).

*Each value is the mean of ten samples per treatment; H1=Harvest 1, H2=Harvest 2.

of control, respectively. Total protein in the stubble was 64, 79, and 70 percent of control for O_3, SO_2, and $O_3 + SO_2$ treatments, respectively. Total protein in the plant roots of each treatment group was approximately 60 percent of control.

The amount of nitrogen in a plant is related to the amount of protein in a plant. Therefore, the same differences shown above for protein are also true for the amount of atmospheric N that was symbiotically fixed and present in the alfalfa tissue.

The dry weight of forage at the first harvest was 69, 54, and 61 percent of control for O_3, SO_2, and $O_3 + SO_2$ treatments, respectively (Figure 7); and at the second harvest, the forage dry weights were further reduced to 51, 50,

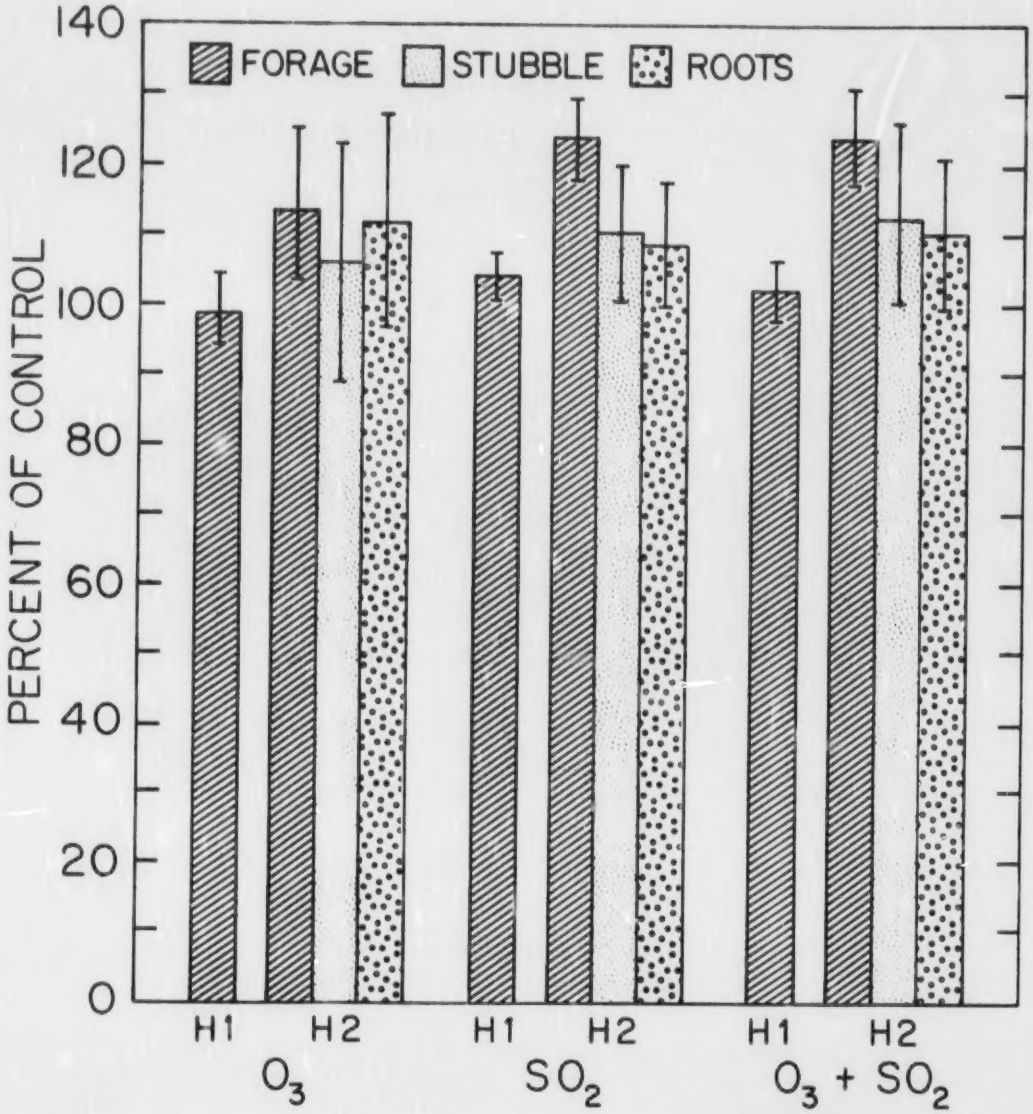

Figure 4. Total protein content of sand alfalfa (unit weight).

and 56 percent of control, respectively. Stubble dry weights for the O_3, SO_2, and O_3 + SO_2 treatments were 61, 72, and 72 percent of control, respectively, while root dry weights were approximately 55 percent of control.

DISCUSSION

The pollutant treatments caused greater reductions (compared to controls) in metabolites produced per sample at successive harvests. This indicates that the plants became less vigorous as the exposure time increased, because the stressed plants had decreasing total metabolite pools for growth.

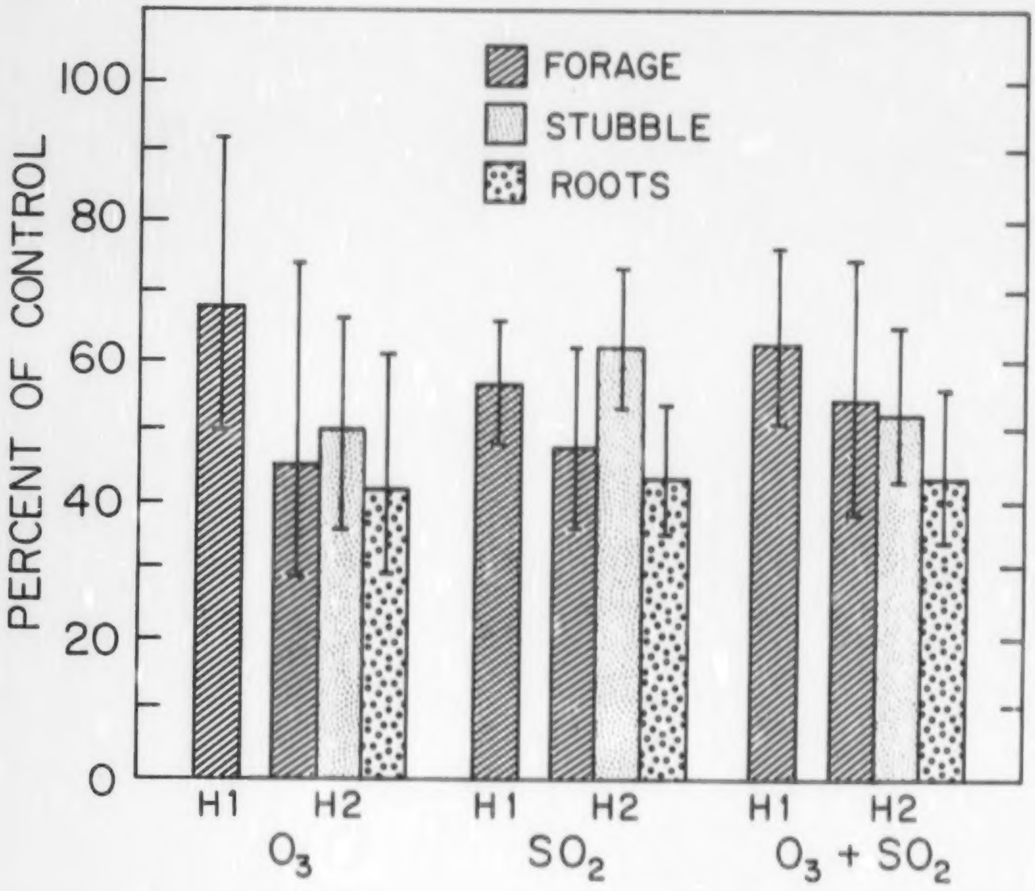

Figure 5. Total nonstructural carbohydrate content of sand alfalfa (total weight).

The early large reduction in yield of the sand alfalfa exposed to pollutants noted at the first harvest was probably caused by these plants being stressed at an early growth stage before metabolite pools were established for later growth. Exposure of alfalfa and perhaps other crops during early growth stages is apparently very damaging to yields.

According to Smith and Silva (13), accumulated carbohydrates in alfalfa roots are primarily used for forage rather than root growth. The greater than 50 percent loss in total TNC stored in the roots of stressed plants at the second harvest of the sand alfalfa experiment indicates that the plant's capacity to produce new top growth had been reduced significantly. Also, loss in root dry weight adversely affects the plant's ability to absorb nutrients needed for growth (14). The reduction in stored carbohydrates and smaller roots in pollutant-treated plants probably accounts for the large reduction noted in both studies. Research on tree species exposed to low levels of ozone also indicated greater reductions in plant dry weights (compared to controls) as the season progressed (15, 16).

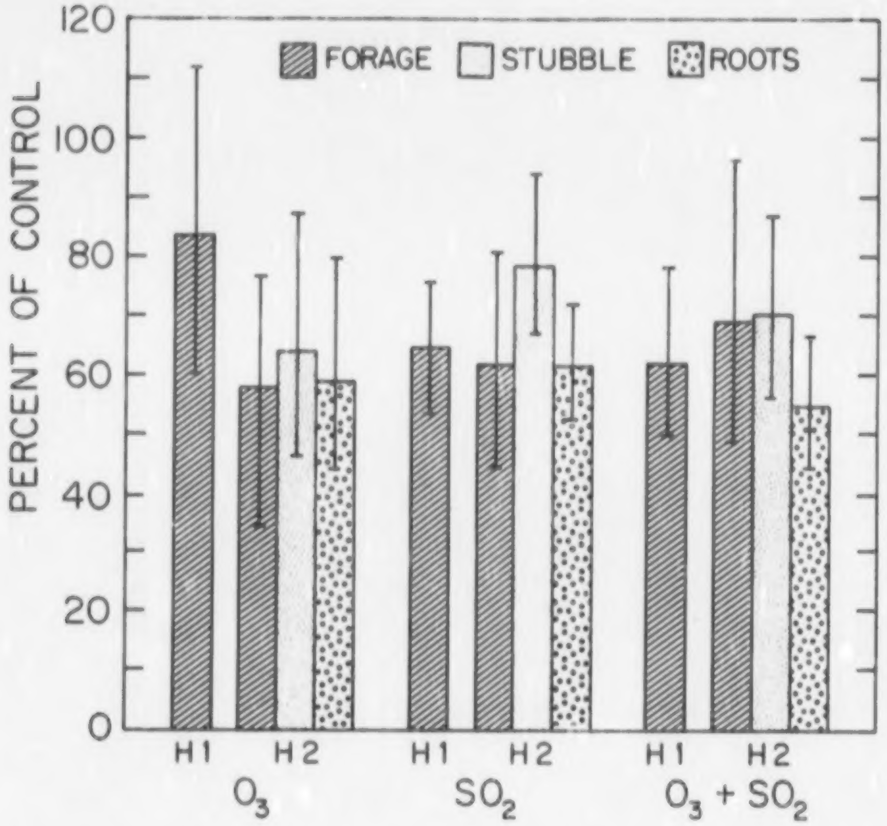

Figure 6. Total protein content of sand alfalfa (total weight).

The greater the protein content, the higher the forage quality. Forage from pollutant-stressed plants tended to be of higher quality than the control. However, there was a net loss in total protein produced per treatment by stressed plants because of the reduced growth. Since N is an important nutrient in plant growth, the considerable loss in total N fixed by pollutant-stressed alfalfa also helps explain reduced growth and yield. Root metabolites are important energy sources for reduction and incorporation of atmospheric N into organic compounds (8). The reduction in N fixed by pollutant-stressed alfalfa was probably caused by reduced quantities of metabolites translocated from the forage to the roots.

The mixture of O_3 and SO_2 did not greatly alter the measured plant responses compared to the effects of single pollutants. This relationship may not exist at higher or lower concentrations of these pollutants. The large reductions in yield and total metabolites produced under long periods of low-level O_3 stress, alone or in combination with SO_2, demonstrates the need for further research to define the yield effects of long-term, low-level oxidant exposures alone and in combination with other pollutants. This information is essential in establishing secondary air quality standards that would minimize crop losses.

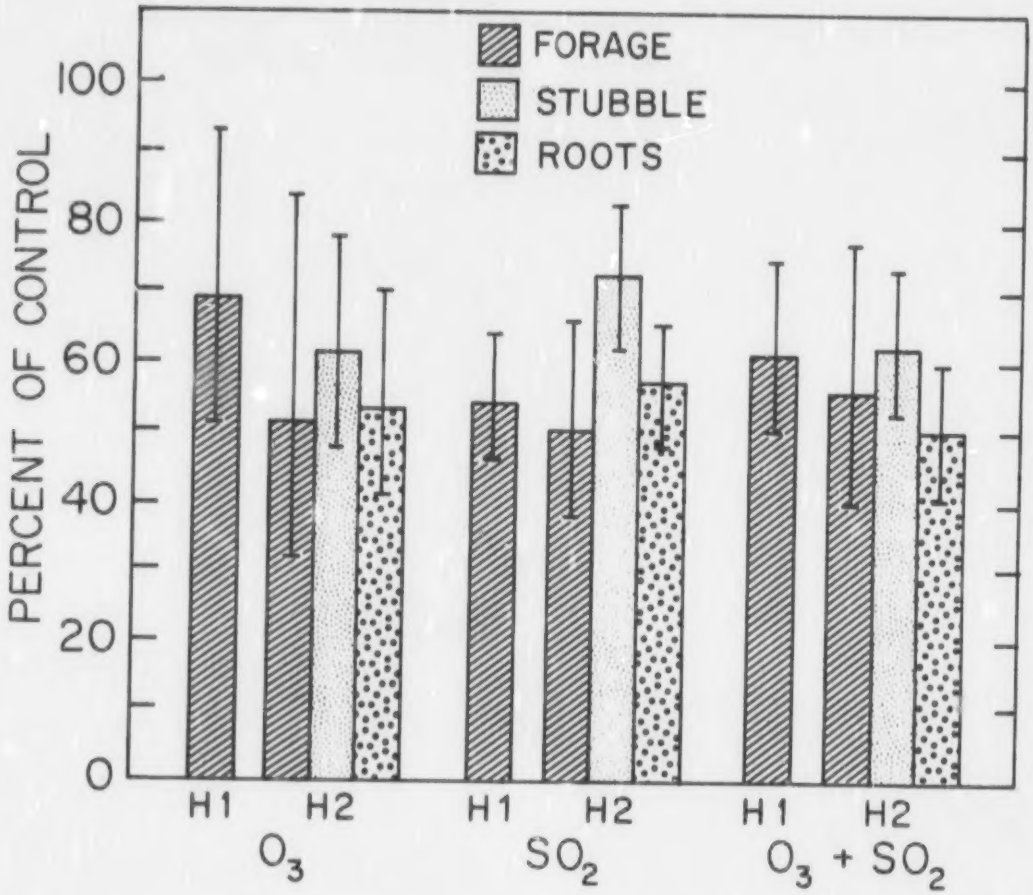

Figure 7. Dry weight of sand alfalfa.

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SESSION 14

REACTIVITY AND ITS USE IN OXIDANT-RELATED CONTROL

Chairman: J.G. Calvert
Ohio State University

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MULTIDAY IRRADIATION OF NO_x-ORGANIC MIXTURES

W. A. Glasson and P. H. Wendschuh*

ABSTRACT

An experimental simulation of urban pollution transport to rural environments was applied to (1) the irradiation of several hydrocarbons and organic solvents and (2) the irradiation of a typical urban hydrocarbon mixture in the presence of varying concentrations of nitrogen oxides. Maximum ozone concentration and ozone dosage were used as measures of oxidant.

It was found that the reactivities of three automotive paint solvents in oxidant formation, although significantly different in the early stages of a 24-hour continuous irradiation, merged by the end of the runs. In the transport simulation experiments, it was found that reactivity is only moderately altered on the second and third days of irradiation. Thus, hydrocarbon reactivity is still an important consideration in controlling organic emissions even in situations involving long-distance transport.

In the nitrogen oxides variation study, the results showed that ozone versus nitrogen oxides plots for each irradiation day displayed the typical nitric oxide-inhibition shape. An analysis of this urban-to-rural transport simulation indicated that reduction of urban nitrogen oxides to control rural oxidant could result in an adverse effect on urban ozone and little effect on rural ozone.

INTRODUCTION

Transport of oxidant and/or oxidant precursors has been suggested as the cause of rural oxidant exceeding the air quality standard of 0.08 ppm(1). A number of factors, including dilution, tend to decrease reactivity differences with increased time. Presumably for this reason, it has been suggested that hydrocarbon reactivity is not an important consideration in controlling oxidant in rural environments in spite of the obvious advantage in urban environments (1). As a test of this suggestion, reactivities in oxidant formation were determined in 24-hour continuous irradiations for three automotive paint solvents and in an experimental simulation of urban-to-rural transport using several hydrocarbons and organic solvents. The simulation consisted of three 6-hour irradiation periods separated by two 6-hour dark periods. Atmospheric dilution was simulated by the nautral leakage from the chamber.

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The results of recent studies have been interpreted to mean that rural oxidant formation is enhanced by increasing nitrogen oxides(2,3). These results lead to the suggestion that reduction of urban NO_x will result in rural oxidant reductions (1). This suggestion was tested by studying the effect of varying NO_x concentration on ozone (O_3) formation in the photooxidation of a hydrocarbon mixture typical of polluted urban atmospheres, using the transport simulation described above in our work, maximum O_3 concentration and O_3 dosage were used as measures of oxidant.

EXPERIMENTAL

The experiments were carried out in a smog chamber which has been described previously (4). Losses due to sampling and leaks were compensated by the addition of dilution air. This dilution air was filtered, passed over an oxidation catalyst, and saturated with water. The dilution rate was 0.0015% sec^{-1} as measured using sulfur hexafluoride (SF_6) as a tracer, leading to 80% loss of reactants in 30 hours. The light intensity corresponded to k_1 = 0.042 sec^{-1}, and the experiments were run at an average temperature and relative humidity of 34°C and 23%, respectively.

Nitric oxide/nitrogen oxides (NO/NO_x) and O_3 were determined continuously by Monitor Labs Model 8440 and McMillan Electronics Corporation Model 1100 chemiluminescent analyzers, respectively. Individual hydrocarbons were determined with a Perkin-Elmer 900 gas chromatograph equipped with dual flame ionization detectors (FID's), using columns described previously (5). Formaldehyde was determined by the chromotropic acid method (6).

RESULTS AND DISCUSSION

HYDROCARBON REACTIVITY

In the first test of long-term irradiation on reactivity, 1.6 ppm of three automotive paint solvents was irradiated with 0.8 ppm NO_x continuously for 24 hours. The results are given in Figure 1. Solvent C (pre-Rule 66) formed the most O_3 in the first six hours of irradiation, followed by solvent B (solvent A + 10% xylenes) and solvent A (exempt). By the end of the 24 hours of irradiation, all the solvents were producing similar amounts of O_3. It is clear, though, that the O_3 dosage experienced in the first six hours is terms of the atmosphere, the urban environment would be exposed to higher O_3 substantially greater for solvent C and, thus, in concentrations in this case. It might be argued that continuous irradiation experiments are unrealistic representations of amtospheric transport processed, due to diurnal variations in light intensity.

We have studied the effect of long-term irradiation of hydrocarbon reactivity using the experimental simulation described above. The results of a typical multiday irradiation expeiment are given in Figure 2 for the irradiation of 1.6 ppm solvent 3600 (C in Figure 1) and 0.8 ppm NO_x. Succeeding irradiation periods show decreasing O_3 and nitrogen dioxide (NO_2) concentrations, while NO is essentially completely oxidized in the first irradiation

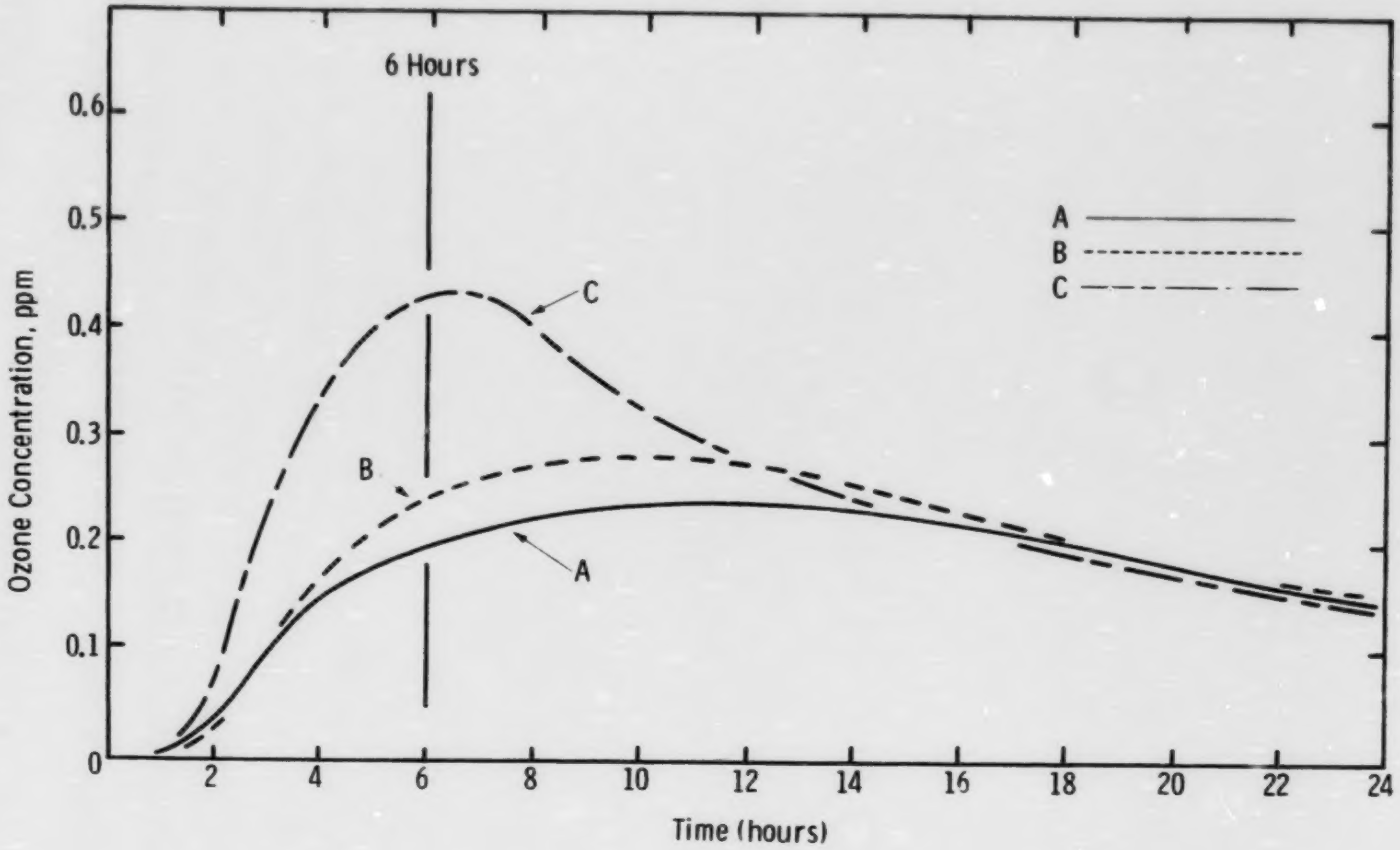

Figure 1. Comparison of Ozone Production from Three Paint Solvent-NO_x Mixtures.

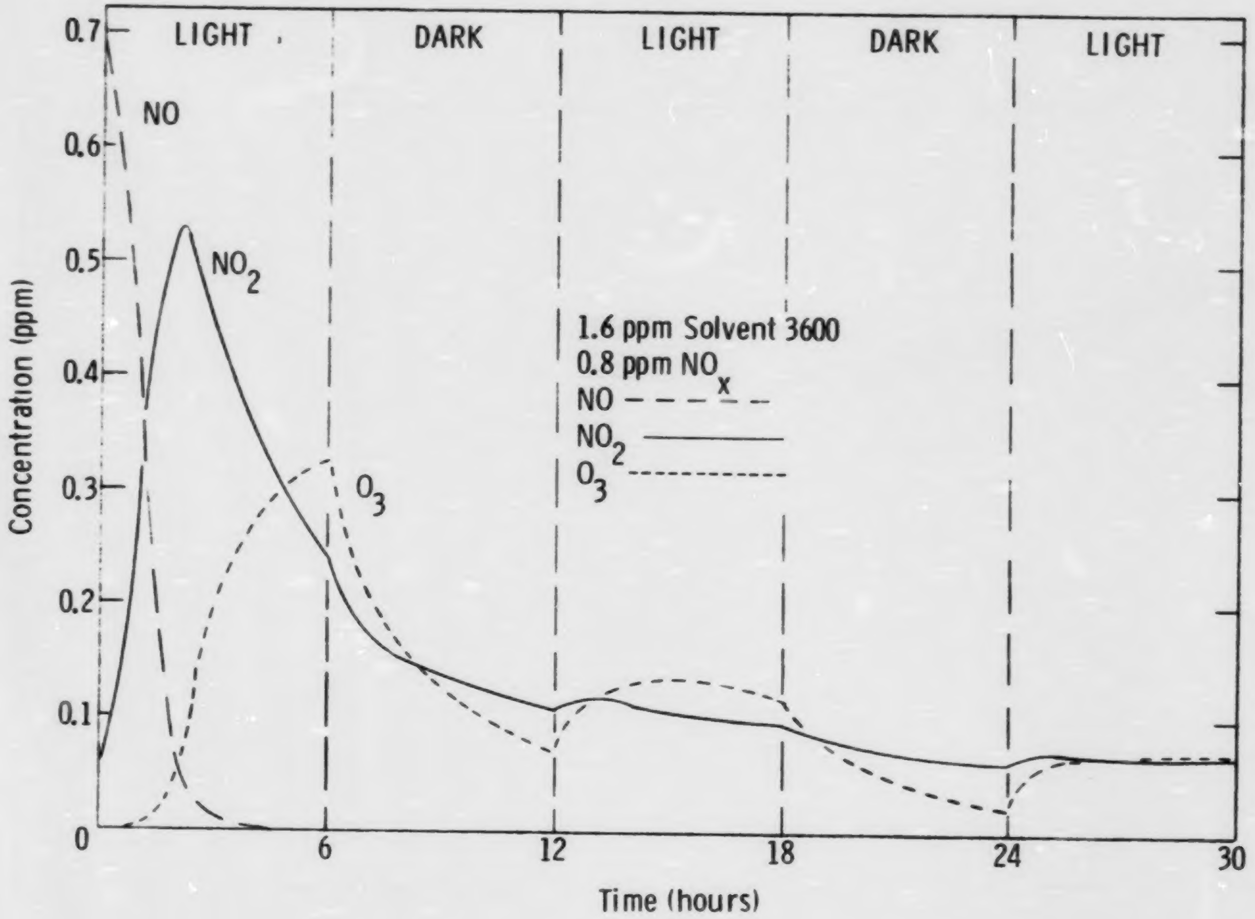

Figure 2. Typical Multiday Irradiation Experiment.

period. Nitrogen dioxide and O_3 decrease in the dark periods due to a combination of dilution, chemical reaction, and wall losses. Ozone concentrations formed in a similar experiment without added hydrocarbon or NO_x can be used as a measure of chamber reactivity. In such an experiment, the irradiation of background concentrations of hydrocarbon and NO_x (0.05 ppm and 0.08 ppm, respectively) produced 0.007, 0.011, and 0.012 ppm O_3 in the first, second, and third irradiation periods, respectively. These values suggest that chamber reactivity is not a significant factor in our experiments.

The results of the irradiation of 1.6 ppm of a series of hydrocarbons, solvents, and auto exhaust with 0.8 ppm NO_x are given in Table 1. In general, in each succeeding irradiation period less O_3 is produced, with the exceptions of n-butane and solvent 3694 (a largely paraffinic solvent). Comparisons of the data of this study with literature data show general agreement within the ranges found in the literature.

TABLE 1. MULTIDAY IRRADIATIONS OF VARIOUS ORGANIC COMPOUND-NO_x MIXTURES

Organic reactant	1st Day	(O_3)max (ppm) 2nd Day	3rd Day
Benzene	0.029	0.016	0.018
Toluene	0.25	0.046	0.029
n-Butane	0.10	0.16	0.077
Propylene	0.47	0.21	0.10
cis-2-Butene	0.43	0.21	0.12
Tetramethylethylene	0.51	0.19	0.063
Trichloroethylene	0.15	0.11	0.041
Solvent 3694	0.15	0.17	0.076
Solvent 3600	0.34	0.13	0.073
Auto exhaust	0.47	0.23	0.13

If differences in hydrocarbon reactivity diminish with irradiation time, then the O_3 concentrations formed in the second and third irradiation periods will show a decreased dependence on the O_3 formed in the first irradiation period. A regression analysis of the data shown in Table 1 displayed correlation coefficients of 0.76 and 0.67 for the second and third irradiation periods, respectively. Thus, although the differences in hydrocarbon reactivity do diminish with irradiation time, the effects of hydrocarbon reactivity on O_3 formation are still apparent after three irradiation "days."

EFFECT OF NITROGEN OXIDES

In the second part of this study, the irradiation of a typical urban hydrocarbon mixture was studied as a function of the NO_x concentration. The average composition of the non-methane hydrocarbon (NMHC) mixture was (%, v/v): ethane, 9.2; ethylene, 11.6; propane, 18.3; propylene, 8.2; n-butane, 23.0; isopentane, 10.3; benzene, 4.4; toluene, 9.8; and m-xylene, 5.3. The average initial NMHC concentration in our experiments was 0.935 ppm, and the reaction mixture also contained an average of 17 ppm carbon monoxide (CO) and 2.8 ppm methane.

The effect of the NO_x concentration at the beginning of each irradiation period on $(O_3)_{max}$ is given in Figure 3. The results show the typical NO-inhibition curve for each irradiation period with the highest $(O_3)_{max}$ occurring at lower NO_x concentrations for each succeeding irradiation period. This effect is undoubtedly due to the lower hydrocarbon concentration present at the start of each succeeding irradiation period. As expected, the olefins are destroyed most rapidly, while the aromatics are destroyed more slowly and the paraffins are destroyed most slowly. The reactivity of the system is supplemented by the presence of the product formaldehyde, and undoubtedly, other aldehydes as well. The average formaldehyde concentrations at the start of the second and third irradiation periods was 0.122 and 0.088 ppm, respectively.

Figure 3 cannot be used to properly evaluate the effect of urban NO_x control on rural ozone since the reduction in NO_x would occur primarily in the urban area. Thus, in Figure 4, O_3 formation for all three periods is plotted against the NO_x concentration at the beginning of the experiment. Again, typical NO-inhibition curves are obtained for the three irradiation periods, except that the NO_x concentration required for maximum O_3 formation increases with each succeeding irradiation day; the latter observation is related to the fact that the NO_x concentration at the beginning of each succeeding irradiation period is not directly proportional to the NO_x concentration at the start of the experiment. The curves suggested that reductions in urban NO_x concentrations will increase O_3 on the first day (urban), slightly reduce O_3 on the second day (rural), and have little effect on O_3 on the third day (rural). Thus, the result of reducing urban NO_x concentrations may be to trade off higher O_3 exposures in the urban population centers for small effects in the sparsely populated rural environment.

Current oxidant control strategy involves hydrocarbon reduction, which should shift the maxima in Figures 3 and 4 to lower NO_x concentrations. It seems likely that the potential benefits of NO_x control will be even more difficult to obtain as hydrocarbon levels are reduced.

It is recognized that the simulation used in the present study is simpler than the atmosphere. Further work is planned to refine the simulation.

Due to space constraints, this report does not include much of the experimental detail. This information can be found in References 6 and 7.

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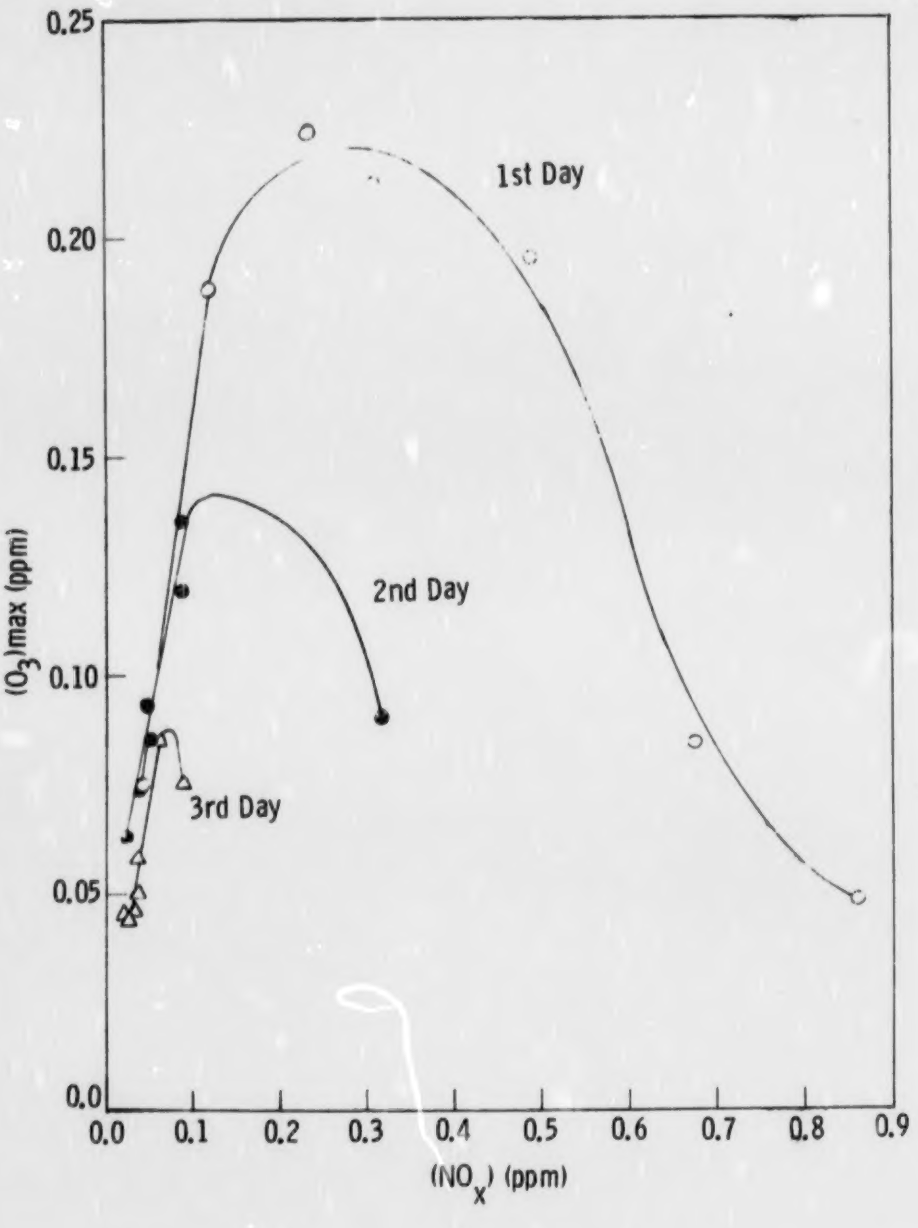

Figure 3. Effect of NO_x on Irradiation of Typical Urban HC Mix.

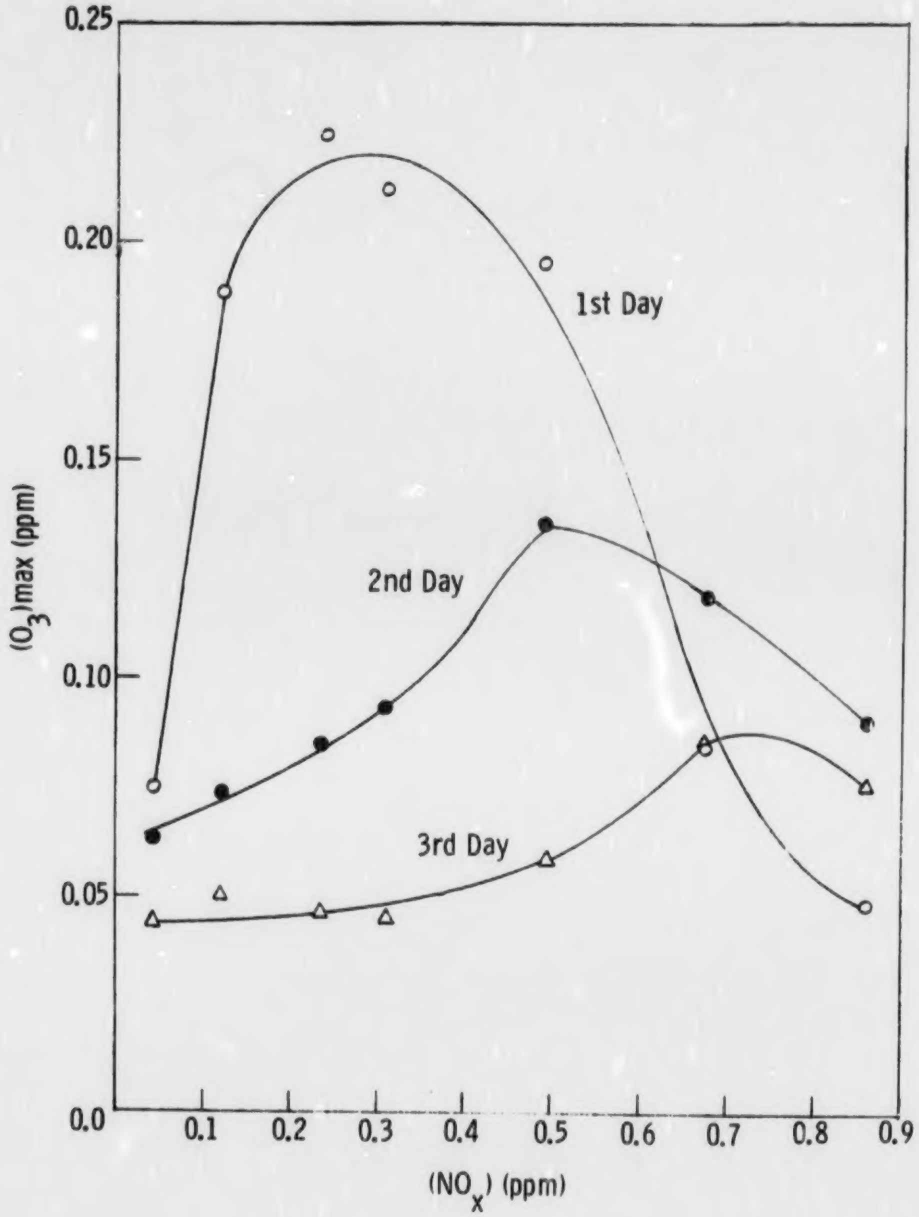

Figure 4. Effect of Urban NO_x on Rural Ozone.

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HYDROCARBON REACTIVITY AND THE ROLE OF HYDROCARBONS, OXIDES OF NITROGEN, AND AGED SMOG IN THE PRODUCTION OF PHOTOCHEMICAL OXIDANTS

J. N. Pitts, Jr., A. M. Winer, K. R. Darnall,
A. C. Lloyd, and G. J. Doyle*

ABSTRACT

A reactivity classification for a broad spectrum of atmospherically important organic (and several inorganic) compounds has been developed. It is based on the rates of reaction of these compounds with the hydroxyl radical, the primary chain carrier in photochemical air pollution and, indeed, in atmospheric chemistry. The classification has been developed in the context of a 5-class reactivity scale in which each class spans an order of magnitude in reactivity relative to methane. An attempt has been made in this paper to incorporate all compounds in the reactivity classification for which hydroxyl radical rate constants have been experimentally determined at room temperature, either by absolute or relative rate techniques. Thus, the present classification contains more than 110 compounds, including alkanes, alkenes, aromatics, oxygenates, natural hydrocarbons, halocarbons, amines, and sulfides. Approximately half of the rate constants employed were determined in this laboratory by either flash photolysis-resonance fluorescence measurements or by relative rate measurements in two $\sim$6000 liter environmental chambers, or by both techniques.

INTRODUCTION

The concept that different hydrocarbons, and their oxygenated and halogenated derivatives, have differing capacities to produce photochemical oxidant orginated some 20 years ago in the classic work of Haagen-Smit and Fox (1). Following contributions by many other workers, this concept has been incorporated in local, state, and federal air pollution control strategies for at least a decade, beginning with the pioneering efforts of the Los Angeles County Air Pollution Control District (LAAPCD). Thus, in 1966, the LAAPCD implemented a regulation known as Rule 66 restricting the composition of organic solvents so as to reduce the use of compounds that were observed to be of the highest reactivity in a major study by LAAPCD workers (2). Since then, while there has been a range of opinion within the scientific community as to the absolute accuracy of predictions of reductions of ambient ozone (O_3) levels based on

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detailed application of such reactivity scales, they have nevertheless received general acceptance as rational and useful elements of cost-effective oxidant control strategies.

Traditionally, such reactivity classifications have been based on smog chamber measurements of various phenomena observed in the photooxidation of hydrocarbon-oxides of nitrogen mixtures under conditions approximating those of polluted ambient atmospheres. These include the rates of hydrocarbon consumption, nitric oxide (NO) to nitrogen dioxide (NO_2) conversion and O_3 formation, as well as maximum levels of O_3 reached, total O_3 dosage, aerosol formation, degree of eye irritation, plant damage, etc. Much of the reactivity data which had been accumulated through 1969 for each of these manifestations (except plant damage) was critically reviewed by Altshuller and Bufalini in 1971 (3). In addition to noting general agreement in reactivity trends obtained in various studies (some employing different reactivity criteria), they cited a number of significant discrepancies in the specific assignments of reactivity to individual compounds and even to whole classes of compounds.

Such differences are not surprising since the observed values of the secondary smog manifestations cited above can be substantially affected by a number of aspects of the smog chamber analytical and experimental methodologies employed. Important factors in this regard are, for example, intensity and spectral distribution of the ultraviolet (UV) light source, surface to volume ratio and nature of the walls and windows of the chamber, specific measurement methods employed for reactants and products, purity of matric air, hydrocarbon (HC) to nitrogen oxides (NO_x) ratios, length of irradiation, etc. Clearly, differences in reactivity scales are not only of concern per se, but also because they can lead to important differences in emission inventories for reactive hydrocarbons and in strategies for their control (4-6).

RECENT DEVELOPMENTS

In 1974 the Environmental Protection Agency (EPA) held a major conference on solvent reactivity. Existing hydrocarbon reactivity data (including those from chamber studies by Battelle, SRI, and Shell) and approaches to formulating hydrocarbon reactivity scales were discussed and evaluated at this conference. Consideration was also given to preliminary evidence then being accumulated concerning the occurrence of pollutant transport and the recognition that such transport will enhance the formation of oxidant from "low reactivity" organics. Data gathered in the succeeding two years has confirmed the necessity for control officials to consider the problems of (a) long-range transport of O_3 and its precursors, and (b) the occurrence of meteorological conditions resulting in multi-day "stagnant air" episodes (leading to persistent high O_3 levels) in which ambient air contains not only each day's fresh pollutant burden but also "aged smog" carryover from the previous day(s). Under each of these conditions, a number of compounds previously cited in some classifications as "nonreactive" or of "low" reactivity--for example, propane and n-butane--can react to produce substantial amounts of O_3.

The oxidant generating capacity, during long irradiation periods, of hydrocarbons (and oxygenates, halogenates, etc.) formerly classified to be "nonreactive" has posed serious problems for regulatory agencies. Control officials are faced with balancing today's serious economic and energy constraints against the need to protect the public from elevated oxidant levels not just in urban centers but also tens to hundreds of kilometers "downwind" of the urban centers where millions of suburbanites reside. Dispersion of urban plumes over long distances also complicates the regulation of hydrocarbon emissions from industries located in suburban and rural areas, since such areas may experience O_3 levels exceeding the Federal Air Quality Standard despite the fact that local industries may not be the major sources of O_3 precursors.

REACTIVITY SCALE BASED ON REACTION WITH HYDOXYL RADICAL

The need for new experimental data sets upon which to base contemporary reactivity classifications has been emphasized by both the EPA and very recently by the California Air Resources Board (ARB) (8). An accepted method of generating the desired information would be a carefully designed environmental chamber study in which the O_3-forming capacity of each of a very large number of organic compounds would be determined under a standard set of simulated atmospheric conditions, including long-term irradiation (i.e., 10-12 hours). Such a program would be extremely time consuming and expensive and would inevitably suffer to some degree from the problems noted in previous chamber studies of this type.

Recently, we have proposed a supplementary (rather than a substitute) approach to obtaining the required data, an approach which does not suffer significantly from the difficulties cited above (although subject to definite limitations which will be discussed). Specifically, we have proposed a hydrocarbon reactivity scale based not on secondary smog manifestation criteria, but rather on the primary chemical act of hydroxyl radical (OH) attack on organic species (9, 10). We have done so on two bases: first, that the OH radical is the most important reactive intermediate in photochemical air pollution, and second, that a reactivity scale based on the depletion of hydrocarbons by reactions with OH has utility in assessing hydrocarbon chemical behavior in polluted ambient air, since only those compounds which participate at "significant" rates in atmospheric reactions are of consequence in the chemical transformations in ambient air, including, of course, the production of photochemical oxidant. Thus, our working premise has been that the relative reactivity of organics towards OH is generally a useful and directly measurable index of their potential importance in the production of secondary pollutants. As we have previously pointed out, however, if specific reactivity criteria unrelated in varying degrees to oxidant formation are of concern--for example, aerosol formation and associated visibility effects, mutagenic activity, etc.--our proposed reactivity classification may or may not have any validity whatsoever (11).

BACKGROUND AND APPLICABILITY OF THE PROPOSED HYDROXYL RADICAL REACTIVITY CLASSIFICATION

The important role of OH in photochemical smog formation is now well established on the basis of both experimental and computer modeling studies (12-20), and OH has been directly observed in both the laboratory and in ambient air (21-23). This awareness has led to a dramatic increase during the past several years in the number of compounds for which OH rate constants have been measured. For example in this laboratory, in addition to extensive absolute rate measurements by flash photolysis-resonance fluorescence (24-34), we have employed two ~6000 liter environmental chambers to measure relative rates, with an accuracy of ±20%, for the reaction of OH with more than 40 compounds under simulated atmospheric conditions of temperature, pressure, concentrations, and light intensity. These relative rate constants were placed on an absolute basis using the published rate constants for OH + n-butane or isobutene. The detailed kinetic data derived from these investigations have been previously reported (34-40). This technique has also been employed recently by Niki and coworkers (41).

From the successful correlation of OH rate constants with the rates of hydrocarbon disappearance observed in chamber simulations at the SAPRC (34-39) and Ford Motor Co. (41) laboratories, we conclude that, to a good approximation, this correlation can be extrapolated to the atmosphere for (a) alkenes in ambient air parcels during the early morning hours when O_3 levels are generally quite low ($\leq$0.05 parts per million (ppm)), and for (b) alkanes, aromatics, and most of the other classes of compounds discussed here at essentially all times and locations. The latter assumption, namely that an OH rate constant is a good "reactivity index" for alkanes, aromatics, halocarbons, etc. throughout an irradiation day (or multiple irradiation days), rests upon the fact that the rates of reaction of these classes of organics with species such as O_3, $O(^3P)$ atoms and the hydroperoxyl radical are several orders of magnitude slower than with OH (42-46). For example, even at the highest ozone concentrations experienced in ambient atmospheres, O_3 will not contribute significantly to the consumption of alkanes and aromatics. This is in contrast to the case for alkenes which, although the rate constants for reaction of O_3 with alkenes are not particularly large (46-48), react rapidly with O_3 at the average concentrations commonly encountered in polluted ambient air (~0.1-0.2 ppm).

Although a reactivity scale based on OH rate constants can, in principle, be divided into a large number of classes, it is convenient, particularly for purposes of comparison with other scales, to use the five-class scale we have previously formulated (10). This scale is based on order of magnitude differences in reactivities of organics toward OH relative to methane (=1). The scale is shown in Table 1. Table 1 also gives the range of half-lives of compounds appearing in each class assuming depletion solely due to reaction with the OH radical at a concentration of 10^7 radicals cm^{-3}. Our initial resulting reactivity classifications, based on available OH rate data in References 9 and 10, contained 80 and 34 organic compounds, respectively. In this paper we attempt to present a reactivity classification which is exhaustive with respect to the reported room temperature literature for OH rate constant determinations (as well as recent, as yet unpublished, measurements in this laboratory). Thus we have compiled a reactivity classification consisting of 113 compounds assigned into the 5 classes of our proposed reactivity scale. Table 2 gives the rate constant (with its source),* the reactivity (relative to methane = 1), and proposed classification for each compound, with the compounds arranged by

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* The rate constant data given in Table 2 are not to be construed as critically evaluated or recommended values. In general, absolute rate determinations were used when available, and average values are often given.

TABLE 1. REACTIVITY SCALE FOR ORGANICS BASED ON RATE OF CONSUMPTION DUE TO REACTION WITH THE HYDROXYL RADICAL

Class	Half-life[a] (days)	Reactivity Relative to Methane (=1)
I	≥ 10	≤ 10
II	1 - 10	10 - 100
III	0.1 - 1	100 - 1000
IV	0.01 - 0.1	1000 - 10,000
V	≤ 0.01	$\geq 10{,}000$

[a] $t_{1/2} = 0.693/k_{OH}[OH]$. [OH] is assumed to be 10^7 radicals cm^{-3}.

chemical class. In view of the growing attention being given to nitrogen- and sulfur-containing compounds in the polluted troposphere, we have included ammonia, methylamine, hydrogen sulfide, and methyl mercaptan in our classification (as well as carbon monoxide as a matter of interest). For convenience, we also present, in Table 3, the compounds appearing in each of the 5 classes of the SAPRC reactivity scale in order of increasing reactivity within each class.

TABLE 2. REACTIVITY CLASSIFICATION OF ORGANICS (AND SELECTED INORGANICS) BASED ON REACTION WITH THE HYDROXYL RADICAL

Compound	k^{a}_{OH+Cpd} (ℓ mol^{-1}s^{-1})x10^{-9}	Reference	Reactivity Relative to Methane = 1	Proposed Class
Alkanes				
Methane	0.0048	64,70,71,74,76	1	I
Ethane	0.17	70,72,76	35	II
Propane	1.3	69,76	270	III
n-Butane	1.8	31,62,68-70,75,78	375	III
Isobutane	1.3	41,70	270	III
Cyclobutane	0.72	69	150	III
n-Pentane	3.9	41	810	III
Isopentane	2.0	36	420	III
Cyclopentane	3.7	79	765	III
Neopentane	0.49	70	100	III
n-Hexane	3.6	36,41,63	750	III
Cyclohexane	4.2	41,69,70	875	III
2-Methylpentane	3.2	36	665	III
3-Methylpentane	4.3	36	900	III
2,3-Dimethylbutane	3.1	39	645	III

(continued)

TABLE 2. (Continued)

Compound	k^{a}_{OH+Cpd} ($mol^{-1}s^{-1}$)$\times10^{-9}$	Reference	Reactivity Relative to Methane = 1	Proposed Class
2,2,3-Trimethylbutane	2.3	39	480	III
2,2,4-Trimethylpentane	2.3	70	480	III
n-Octane	5.1	70	1060	IV
2,2,3,3-Tetramethylbutane	0.67	70	140	III
Alkenes				
Ethene	4.7	33	985	III
Propene	15.1	27	3145	IV
1-Butene	21.3	27	4440	IV
Isobutene	30.5	27	6355	IV
cis-2-Butene	32.3	27	6730	IV
trans-2-Butene	42.1	27	8770	IV
1-Pentene	18	41	3750	IV
cis-2-Pentene	39	41	8125	IV
2-Methyl-1-butene	35	41	7290	IV
2-Methyl-2-butene	48	29	10,000	V
1-Hexene	19	41	3960	IV
Cyclohexene	43	39,41	8960	IV
2,3-Dimethyl-2-butene	92	75	19,170	V
3,3-Dimethyl-1-butene	17	41	3540	IV
1-Methylcyclohexene	58	39	12,080	V
1-Heptene	22	39	4585	IV
Di-Alkenes				
Allene	2.7	61	560	III
1,3-Butadiene	46.4	36	9,670	IV
Isoprene	47	37	9,790	IV
Alkynes				
Acetylene	0.099	66	21	II
Methylancetylene	0.57	61	120	III
Aromatic Hydrocarbons				
Benzene	0.85	25,65	180	III
Toluene	3.6	25,65	750	III
n-Propylbenzene	3.7	36	770	III
Isopropylbenzene	3.7	36	770	III
Ethylbenzene	4.8	36	1000	IV
p-Xylene	7.4	25,35	1540	IV
o-Xylene	8.4	25,35	1750	IV
m-Xylene	14.1	25,35	2940	IV
p-Ethyltoluene	7.8	36	1625	IV
o-Ethyltoluene	8.2	36	1710	IV
m-Ethyltoluene	11.7	36	2440	IV
p-Cymene	9.2	37	1920	IV
1,2,3-Trimethylbenzene	14.9	25,35	3100	IV
1,2,4-Trimethylbenzene	20	25,35	4170	IV
1,3,5-Trimethylbenzene	29.7	25,35	6190	IV

(continued)

TABLE 2. (Continued)

Compound	k^{a}_{OH+Cpd} ($mol^{-1}s^{-1}$)x10^{-9}	Reference	Reactivity Relative to Methane = 1	Proposed Class
Ketones				
Methyl ethyl ketone	2.0	37	420	III
Methyl isobutyl ketone	9.0	37	1875	IV
Diisobutyl ketone	15	37	3125	IV
Alcohols				
Methanol	0.57	63	120	III
Ethanol	1.8	63	375	III
n-Propyl Alcohol	2.3	63	480	III
Isopropyl Alcohol	4.3	38	895	III
n-Butanol	4.1	63	855	III
4-Methyl-2-pentanol	4.3	73	895	III
Ethers				
Diethyl ether	5.6	38	1170	IV
Di-n-propyl ether	10.4	38	2170	IV
Tetrahydrofuran	8.8	40	1830	IV
Esters				
n-Propyl acetate	2.7	40	560	III
sec-Butyl acetate	3.4	40	710	III
Natural Hydrocarbons				
α-Pinene	35	37	7290	IV
β-Pinene	41	37	8540	IV
p-Menthane	4	37	830	III
3-Carene	52	37	10,830	V
α-Phellandrene	70	37	14,580	V
Carvomenthene	76	37	15,830	V
d-Limonene	90	37	18,750	V
Dihydromyrcene	101	37	21,040	V
Myrcene	137	37	28,540	V
cis-Ocimene	192	37	40,000	V
Halocarbons				
Fluoromethane	0.0096	71	2	I
Chloromethane	0.025	28,67,71	5	I
Bromomethane	0.023	67,71	5	I
Difluoromethane	0.0047	71	1	I
Chlorofluoromethane	0.022	71	5	I
Dichloromethane	0.084	28,67,71	18	II
Trifluoromethane	0.00012	71	0.025	I
Chlorodifluoromethane	0.025	26,71	5	I
Dichlorofluoromethane	0.016	28,71	3	I
Trichloromethane	0.065	67,71	14	II
Tetrafluoromethane	<0.00024	71	<0.05	I
Chlorotrifluoromethane	<0.00042	71	<0.09	I

(continued)

TABLE 2. (Continued)

Compound	k^{a}_{OH+Cpd} (ℓ $mol^{-1}s^{-1}$)x10^{-9}	Reference	Reactivity Relative to Methane = 1	Proposed Class
Dichlorodifluoromethane	<0.0006	26,71	<0.13	I
Fluorotrichloromethane	<0.0006	26,71	<0.13	I
Tetrachloromethane	<0.0024	71	<0.5	I
Chloroethane	0.235	72	49	II
1,2-Dichloroethane	0.132	72	28	II
1,2-Dibromoethane	0.15	72	31	II
1,1-Difluoroethane	0.019	72	4	I
1,1-Dichloroethane	0.16	72	33	II
1-Chloro-1,1-difluoroethane	0.0017	72	0.35	I
1,1,1-Trichloroethane	0.0090	72	2	I
1,1,1-Trifluoro-2-chloroethane	0.0063	72	1	I
1,1,1,2-Tetrafluoro-2-chloroethane	0.0075	72	2	I
1,1,1-Trifluoro-2,2-dichloroethane	0.0171	72	4	I
1,1,2,2-Tetrafluoro-1,2-dichloroethane	<0.0003	72	<0.06	I
1,1,2-Trifluoro-1,2,2-trichloroethane	<0.0002	72	<0.04	I
Nitrogen-Containing Compounds				
Ammonia	0.0988	30	21	II
Methylamine	13.2	77	2750	IV
Sulfur-Containing Compounds				
Hydrogen sulfide	3.16	30	660	III
Methyl mercaptan	20.4	77	4250	IV
Miscellaneous				
Carbon monoxide	0.084	46	18	II
Methoxybenzene	11.8	77	2460	IV
o-Cresol	20.5	77	4280	IV

[a] "Room temperature" (i.e., within range 292-305 K).

COMPARISON WITH OTHER REACTIVITY CLASSIFICATIONS

In our proposed reactivity classification, Class I contains methane and most halocarbons. The remaining half-dozen halocarbons appear in Class II along with carbon monoxide, ammonia, acetylene and ethane. Almost all alkanes appear in Class III while alkenes other than ethene appear in Classes IV or V. Aromatics and oxygenates appear in Classes III or IV and the natural hydrocarbons (not specifically identified in previous reactivity classifications) are of high reactivity and appear in Classes IV and V. Clearly, our proposed classification emphasizes that most compounds react in polluted atmospheres and Classes I and II contain the relatively few compounds which have half-lives greater than 10 days and 24 hours, respectively. This result parallels the conclusion by

TABLE 3. PROPOSED REACTIVITY CLASSIFICATION OF ORGANICS (AND SELECTED INORGANICS) BASED ON REACTION WITH THE HYDROXYL RADICAL

Class I ($\leq 4.8\text{x}10^7$)[a]	Class II ($4.8\text{x}10^7$ - $4.8\text{x}10^8$)[a]	Class III ($4.8\text{x}10^8$ - $4.8\text{x}10^9$)[a]	Class IV ($4.8\text{x}10^9$ - $4.8\text{x}10^{10}$)[a]	Class V ($\geq 4.8\text{x}10^{10}$)[a]
Trifluoromethane	Trichloromethane	Neopentane	Ethylbenzene	2-Methyl-2-butene
1,1,2-Trichloro-1,2,2-trifluoroethane	Dichloromethane	Methanol	n-Octane	3-Carene
Tetrafluoromethane	Carbon monoxide	Methylacetylene	Diethyl ether	1-Methylcyclohexene
1,2-Dichloro-1,1,2,2-tetrafluoroethane	Ammonia	2,2,3,3-Tetramethylbutane	p-Xylene	β-Phellandrene
Chlorotrifluoromethane	Acetylene	Cyclobutane	p-Ethyltoluene	Carvomenthene
Dichlorodifluoromethane	1,2-Dichloroethane	Benzene	o-Ethyltoluene	d-Limonene
Fluorotrichloromethane	1,2-Dibromoethane	Isobutane	o-Xylene	2,3-Dimethyl-2-butene
1-Chloro-1,1-difluoroethane	Ethane	Propane	Tetrahydrofuran	Dihydromyrcene
Tetrachloromethane	1,1-Dichloroethane	n-Butane	Methyl isobutyl ketone	Myrcene
Difluoromethane	Chloroethane	Ethanol	p-Cymene	cis-Ocimene
Methane		Methyl ethyl ketone	Di-n-propyl ether	
2-Chloro-1,1,1-trifluoroethane		Isopentane	m-Ethyltoluene	
2-Chloro-1,1,1,2-tetrafluoroethane		1-Propanol	Methoxybenzene	
1,1,1-Trichloroethane		2,2,4-Trimethylpentane	Methylamine	
Fluoromethane		2,2,3-Trimethylbutane	m-Xylene	
Dichlorofluoromethane		n-Propyl acetate	1,2,3-Trimethylbenzene	
2,2-Dichloro-1,1,1-trifluoroethane		Allene	Diisobutyl ketone	
1,1-Difluoroethane		2,3-Dimethylbutane	Propene	
Chlorofluoromethane		Hydrogen sulfide	3,3-Dimethyl-1-butene	
Bromomethane		2-Methylpentane	1-Pentene	
Chloromethane		sec-Butyl acetate	1-Hexene	
Chlorodifluoromethane		Toluene	1,2,4-Trimethylbenzene	
		Cyclopentane	Methyl mercaptan	
		n-Propylbenzene	o-Cresol	
		Isopropylbenzene	1-Butene	
		n-Hexane	1-Heptene	
		n-Pentane	1,3,5-Trimethylbenzene	
		p-Menthane	Isobutene	
		1-Butanol	cis-2-Butene	
		Cyclohexane	2-Methyl-1-butene	
		2-Propanol	α-Pinene	
		4-Methyl-2-pentanol	cis-2-Pentene	
		3-Methylpentane	β-Pinene	
		Ethene	trans-2-Butene	
			Cyclohexene	
			1,3-Butadiene	
			Isoprene	

[a] Range of values (in liter mole^{-1} sec^{-1}) for the rate constant for reaction of the OH radical with the listed compounds.

Altshuller and Bufalini in their 1971 review article that "almost every hydrocarbon except methane can produce some oxidant when photooxidized in the presence of high enough ratios of hydrocarbons to oxides of nitrogen" (3).

Although our proposed reactivity scale and classification is based solely on consumption rates of organics, Altshuller and Bufalini have shown that this measure of reactivity is very similar to one based on nitric oxide oxidation rates (3). They showed that the ranking of reactivities of hydrocarbons from the nitric oxide photooxidation studies of Altshuller and Cohen (49) and Glasson and Tuesday (42) was essentially the same as that obtained from the studies of hydrocarbon consumption carried out by Schuck and Doyle (50), Stephens and Scott (51), and Tuesday (52). The ranking of reactivities for the aromatic hydrocarbons in our classification is very similar to that obtained by Altshuller et al. (53) and by Kopczynski (54, 55). We have previously shown that our classification (9, 10) is in general agreement with that proposed by Dimitriades (7) in 1974 and noted where significant differences existed. Several of these differences arose from the greater degree of differentiation in reactivity permitted by the OH reactivity criterion.

A three-class reactivity classification of organic compounds very recently adopted by the ARB (56) is shown in Table 4, and is similar to one now under consideration by the EPA (57). As described by the ARB (56, 57), Class I includes low reactivity organic compounds, yielding little if any ozone under urban conditions. Class II consists of moderately reactive organic compounds which give an intermediate yield of O_3 within the first day of solar irradiation, while Class III is limited to highly reactive organic compounds which give high yields of O_3 within a few hours of irradiation.

In general, the ARB three-tiered classification is consistent with the reactivity classification presented here, based on OH rate constants, with only minor exceptions. For example, the ARB scale shows the primary and secondary C_{2+} alcohols to be highly reactive in Class III, while our scale shows them to be of moderate reactivity.

ADVANTAGES AND LIMITATIONS OF THE HYDROXYL RADICAL REACTIVITY CLASSIFICATION

In contrast to previous reactivity scales, where it is commonly recognized that uncertainties in the chamber data upon which they are based limit the number of classes into which the reactivity scales can be meaningfully divided (7, 57) our OH reactivity scale could be divided into a large number of classes based on the fact that the general accuracy of OH rate constant measurements is better than ±20%. Thus, one significant strength of this approach is the very high degree of resolution obtained in ranking compounds in order of their rate of reaction with OH. A second advantage of the present classification is that it can be readily extended to include additional organic (and inorganic) compounds once their rate of reaction with OH is known. Thus, it is not necessary to conduct a major new experimental program each time a significant number of new compounds become of interest (as has been felt necessary in the usual smog chamber approach, in order to obtain consistent data for all compounds of interest at a given time). Finally, our proposed classification gives greater weight than most previous classifications to the alkanes and aromatic hydro-

TABLE 4. CALIFORNIA AIR RESOURCES BOARD (ARB) REACTIVITY CLASSIFICATION OF ORGANIC COMPOUNDS[†] (56)

Class I (Low Reactivity)	Class II (Moderate Reactivity)	Class III (High Reactivity)
C_1-C_2 Paraffins	Mono-tert-alkyl-benzenes	All other aromatic hydrocarbons
Acetylene	Cyclic ketones	All olefinic hydrocarbons (including partially halogenated)
Benzene	Alkyl acetates	Aliphatic aldehydes
Benzaldehyde	2-Nitropropane	Branched alkyl ketones
Acetone	C_{3+} Paraffins	Cellosolve acetate
Methanol	Cycloparaffins	Unsaturated ketones
Tert-alkyl alcohols	n-Alkyl ketones	Primary & secondary C_{2+} alcohols
Phenyl acetate	N-Methyl pyrrolidone	Diacetone alcohol
Methyl benzoate	N,N-Dimethyl acetamide	Ethers
Ethyl amines	Alkyl phenols*	Cellosolves
Dimethyl formamide	Methyl phthalates**	Glycols*
Perhalogenated Hydrocarbons		C_{2+} alkyl phthalates**
Partially halogenated paraffins		Other esters**
Phthalic anhydride**		Alcohol amines**
Phthalic acids**		C_{3+} Organic acids + di acid**
Acetonitrile*		C_{3+} di acid anhydrides**
Acetic acid		Formin** (Hexa methylene-tetramine)
Aromatic amines		Terpenic hydrocarbons
Hydroxyl amines		Olefin oxides**
Naphthalene*		
Chlorobenzenes*		
Nitrobenzenes*		
Phenol*		

[†] This reactivity classification is identical to that suggested by the EPA in August, 1975 (see text of References 56 and 57) except that the ARB has moved propane from Class I to Class II. *Reactivity data are either nonexistent or inconclusive, but conclusive data from similar compounds are available; therefore, rating is uncertain but reasonable. **Reactivity data are uncertain.

carbons, which as discussed above, require a longer irradiation period but can, during downwind transport or stagnant air episodes, contribute significantly to O_3 formation.

In closing, we note several caveats which should be borne in mind in applying the proposed OH reactivity scale. First of all, it is not strictly applicable to compounds which undergo significant photodissociation in the atmosphere (e.g., aliphatic aldehydes) or which react in the atmosphere at significant rates with species other than OH (e.g., the alkenes with O_3). In such cases, the compound will be more reactive than predicted from a scale based on consumption due solely to OH attack. It is interesting to note, however, that with respect to the reaction of O_3 with alkenes this limitation is not as serious as it would appear to be based only on the relative rates of consumption of alkenes by O_3 and OH, respectively. This follows from the fact that recently Niki and coworkers (58) have shown that O_3-alkene reactions do not lead predominantly to radical products, and hence this additional alkene consumption pathway will contribute significantly less "additional reactivity" (over that obtained for OH reaction alone) than if it led to radical chain propagation.

A second, and perhaps more significant, limitation in the application of our reactivity classification concerns the inherent problem arising from uncertainties in the identity and fates of subsequent products (7). For example, two compounds which have the same rate constant for reaction with OH may not necessarily have the same oxidant-producing potential in undergoing complete photooxidation. As another example, we have recently reported that the higher alkanes ($\geq C_4$) undergo alkoxy radical isomerization (59), and also that reaction of alkylperoxy radicals ($\geq C_4$) with NO leads to alkyl nitrate formation rather than to $RO + NO_2$ (60). Thus, estimates of O_3 formation (or other secondary smog manifestations) for the higher alkanes which are based soley on their rates of reaction with OH are likely to be somewhat high. These limitations notwithstanding, the reactivity classification presented here should be of utility in assessing the potential contributions of a wide variety of organics to the production of photochemical oxidants.

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DISCLAIMER

The contents do not necessarily reflect the views and policies of the ARB or the NSF-RANN, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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APPLICATION OF REACTIVITY CRITERIA IN OXIDANT-RELATED EMISSION CONTROL IN THE USA

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ABSTRACT

The use of the reactivity criterion in oxidant-related emission control is reexamined in the light of recent research findings on pollutant transport and on oxidant chemistry. Occurrence of pollutant transport is interpreted to dictate that reactivities of organics be measured under longer irradiation and greater organic-to-nitrogen-oxides ratio conditions than previously thought. Reactivities under such conditions have been measured by the Environmental Protection Agency for several organics and results are used here to support a new two-class reactivity classification of organic emissions. Problems associated with the smog chamber measurement of such reactivities and with the use of kinetic indices of reactivity are discussed.

INTRODUCTION

The reactivity concept was born out of early laboratory studies that showed that organic emissions vary widely with respect to their ability to cause photochemical oxidant formation in the ambient air. As of today, the concept has been in use in control practices in the U. S. in the form of regulations calling for selective control of organic solvent emissions. The best known of these regulations is the Rule 66 (1). It was designed for use in Los Angeles, but it was adopted -- intact or slightly modified on -- by several air pollution agencies outside California. The Federal Government has issued a drastically different guideline for use of the reactivity concept (2), but has not objected to the use of Rule 66 by the various State and local governmental agencies. Both the Rule 66 and the Federal Government guideline are not entirely consistent with the latest scientific evidence regarding the role of organic emissions in the ambient oxidant problem (3).

In their present form, these regulations impose two limits to organic solvent emissions: a high limit (e.g. 3000 lb/source/day) for the nonreactive emissions and a low limit (e.g. 15 or 40 lb/source/day) for the reactive ones. Enforcement of two such limits means that the thrust of the regulatory measures is not so much toward emission reduction as it is toward substitution of nonreactive emissions for reactive ones. In fact, in theory at least, these regulations could cause an increase in the amounts of emissions discharged into the atmosphere. This possibility is now thought to have some adverse consequences.

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Because of these problems, the United States Environmental Protection Agency (USEPA) is in the process of reexamining the use of the reactivity concept, in the light of the considerable research findings reported in the last 4 to 5 years. The following is a presentation and discussion of some thoughts that evolved out of such a reexamination.

REASSESSMENT OF THE USE AND UTILITY OF THE REACTIVITY CONCEPT

RECENT RESEARCH FINDINGS AND IMPLICATIONS

There are two aspects of the reactivity issue that need to be reexamined. First, there is the question of whether or not application of the reactivity concept has thus far been demonstrably beneficial. The second aspect pertains to the relative roles of the "reactive" and "nonreactive" organics when such organics are subjected to pollutant transport conditions. These aspects need to be reexamined both separately and in conjunction.

Recent air quality data in the U.S. have indicated that in some localities the air quality improved, in others it deteriorated, and in others it showed no effect in the years since the initiation of emission control. From detailed studies of the impact of emission control on oxidant air quality (4,5), it can be deduced that the impact of the reactivity-related solvent control regulations cannot be directly assessed. This is simply because such impact is masked by the overwhelming effects of other factors such as a reduction in organic auto emission (which is indiscriminate rather than reactivity-related), an increase in nitrogen oxides emissions, growth and/or shifting of human activities, etc. The judgement submitted here is that the impact of any reactivity-related control measure upon air quality can be assessed only indirectly based on laboratory evidence; direct atmospheric observation is inconclusive.

The second aspect of the reactivity issue, the one that deals with the relative roles of the "reactives" and "unreactives," likewise can be examined only indirectly based on laboratory evidence. Relative contributions of the "reactive" and "unreactive" organics to ambient oxidant and, in general, the relative roles of such pollutants cannot be determined from aerometric data.

In conclusion, laboratory evidence -- that is, smog chamber evidence -- with all its uncertainties arising from its indirect nature, continues to provide the only basis for reassessing the use and utility of the reactivity concept. For such a reassessment, therefore, it is necessary first that the recent laboratory evidence be presented and critically examined.

Recent evidence relevant to the issue consists mainly of smog chamber data suggesting that, under the relatively high organic-to-NO_x ratio and prolonged irradiation conditions prevailing in transported air masses, many of the thought-to-be unreactive organics could, in fact, cause significant oxidant buildup (6,7). This is illustrated by the reported data (6,7) and more pointedly by the data of Table 1, obtained from an on-going EPA study. These interpretations, however, of the recent smog chamber data and associated conclusions have been questioned by some investigators on grounds related to the smog chamber background contamination problem. Specifically, it has been claimed that, in general, nonreactive organics exhibit enhanced reactivity in smog chambers because of the presence of a substantial background of hydroxyl (OH) radicals in such chambers (8). Furthermore, such OH concentrations, were estimated (from the EPA data on methane (CH_4) disappearance) to be 1.5 x 10 - 1.7 x 10^8 molecule/cm^3; that is, they were comparable to or higher than the concentrations observed in the real atmosphere (8).

Such claims, although qualitatively correct, do not invalidate the original interpretation of the recent smog chamber data, namely, that under optimum conditions many of the thought-to-be unreactive organics can in fact cause significant ozone (O^3) buildup. To explain, consider all possible situations that cause chamber background OH buildup. First, background OH could form from photolysis of nitrogen-compounds desorbing off the chamber walls. Such a source, however, is unlikely to be important relative to the source created by the NO_x reactant itself in the chamber. Second, and more likely, background OH could form from photochemical reactions of wall-desorbed organics (and inorganics) and the NO_x reactant. However, considering that such desorbed organics are at almost immeasurably low concentrations, it may be deduced that this source of OH is also unavoidably present in the real atmosphere as natural background contamination. Alternatively, the bias caused by the background OH radical problem can be reduced -- but not eliminated -- by subtracting from measured reactivity values the background air reactivity. Finally, irrespective of the chamber background OH problem, it has been established that conditions of prolonged irradiation and an optimum organic-to-NO_x ratio do enhance the reactivities of the less reactive organics.

In conclusion, the laboratory evidence suggests that in consideration of the pollutant transport phenomenon, the existing reactivity classification of organics should be revised so as to reclassify most of the "unreactive" organics into the single class of "reactives." The question of precisely where the borderline should be separating the two classes is a crucial but extremely complex one, and it cannot be answered definitively based on the evidence presently available unless some simplifying assumptions are made. In answer to this question, these authors offer one procedure for defining the boundary between reactives and unreactives. This procedure is based on use of reactivity data obtained in an appropriate chamber under optimum irradiation time and reactant organic-to-NO_x ratio conditions. This procedure is intended to identify as "nonreactive" those organics which under no circumstances will yield oxidant/O_3 concentrations exceeding 0.08 parts per million (ppm). This procedure is illustrated in the next section, using the data of Table 1. Note, however, that the conditions under which these data were obtained may not be the optimum ones. Additional tests using a variety of organic-to-NO_x ratio conditions should be made -- upon the least reactive organics only -- in order to obtain the requisite "optimum " values.

REVISED REACTIVITY CLASSIFICATION

From the data of Table 1, it would appear rational at first glance that the boundary point separating the reactive organics from the unreactive ones should be the reactivity value for propane. Such a judgment, however, presupposes that a 4 ppm/0.2 ppm mixture of propane/NO_x would yield the same concentration of O_3 in the real atmosphere as in EPA's smog chamber.

TABLE 1. REACTIVITIES OF ORGANICS MEASURED IN THE EPA SMOG CHAMBER[a] (11)

Reactant Organic[b]	Maximum O_3 conc., ppm[c]	Peak-O_3 time, hrs	Average rate of organic disappearance, % per hr[d]
Background air	0.03[c]	--	--
Background air + 0.2 ppm NO_x	0.01	--	--
Methane	0	31	0.05
Acetonitrile	0	28	0.02
Benzaldehyde	0	3.1	2.4
1,1,1-trichloroethane	0	4.6	0.1
Chloroform	0	2.4	0.8
Benzene	0.02	1.5	3.1
Methylenechloride	0.03	1.8	5.7
Ethane	0.03	3.0	0.5
Propane	0.08	3.6	2.0
Acetylene	0.10	5.3	6.3
Isobutyl acetate	0.18	4.3	4.3
Acetone	0.18	12.1	0.9
n-Butane	0.23	11.9	1.4
Methanol	0.25	12.3	1.3
Acetic Acid	0.26	13.7	2.0
t-Butanol	0.28	13.8	1.1
Methyl ethyl ketone	0.30	8.3	1.5
i-Propanol	0.32	8.6	3.3
Acrylonitrile	0.37	5.5	5.3
Perchloroethylene	0.49	1.8	12.8

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[a] Chamber was a 400-liter Pyrex glass cylinder irradiated externally with 22 Blacklight and 7 Sunlamp fluorescent lamps.

[b] Initial reactant concentrations were 4.0 ppm and 0.2 ppm for the organic and NO_x, respectively. Each organic was tested at least in duplicate. Irradiation was continued until O_3 peaked out.

[c] Reported data represent observed maximum O_3 concentrations less the maximum O_3 concentration observed for background air (0.03 ppm).

[d] Corrected for dilution. Perchloroethylene, methylene chloride, and chloro form showed considerably higher rates of disappearance after peaking of O_3.

[e] Value represents highest O_3 yield observed in 6 replicated tests randomly dispersed within the reactivity measurement program.

While the above presupposition may or may not be correct -- it can never be checked directly -- the uncertainties involved are not necessarily prohibitive. Comparison of the smog chamber and natural sunlight radiation data indicates that the light intensity in the EPA chamber is comparable to that of natural sunlight. Note that small differences in the radiation factor between smog chamber and real atmosphere are of no serious consequence because, for low reactivity systems, such differences affect mainly the peak-O_3 time and very little the maximum O_3 concentration. The effect on peak-O_3 time, however, (assuming "unlimited" irradiation time under pollutant transport conditions) should not cause the reactivity measurement results to be drastically different than those in Table 1. Relevant important factors, other than radiation, are the chamber background contamination, the chamber wall surface, and dilution. The contamination problem has already been discussed; adjusting the reactivity measurement by subtracting the background air reactivity is simplistic but probably the most acceptable solution to this problem. Thus, for example, after such adjustment, the chamber reactivity of methane is zero, essentially in agreement with the photochemical model predictions (8,9). Furthermore, the surface of the EPA chamber (Pyrex glass) is not expected to alter drastically the dominant steps of the oxidant formation process. Finally, dilution in the smog chamber tests may not be as intensive as in ordinary real atmospheres. However, the difference can be tolerated with the justification that (a) it is not believed to be extremely large, and (b) it makes the chamber data represent the "most unfavorable" situation, a situation often used in control deliberations.

Summarizing the reasoning in the preceding paragraph, the smog chamber reactivities listed in Table 1 should not be drastically different than those expected to be manifested in the real atmosphere. This means that the suggestion that the propane reactivity is the boundary point separating the "reactives" from the "unreactives" would not be grossly wrong. Furthermore, whatever overall error exists is probably in the direction that will produce high reactivity values, that is, a downward misplacement of the boundary point. Fortunately, however, raising the boundary point above the propane reactivity value, e.g., by as much as 100% (i.e., to 0.16 ppm O_3), does not seem to produce a much different classification because the 0.08-0.16 ppm interval is not expected to be densely "populated" by reactivity values of organics. Thus, for example, all halogenated paraffins are expected to have reactivities comparable to those of chloroform, methylene chloride, and 1,1,1-trichloroethane (i.e., below that of propane), whereas all alcohols, ketones, acids and esters are expected to be comparable to or more reactive than acetone, methanol, and acetic acid, (i.e., much more reactive than propane). These expectations, of course, need to be verified by testing commonly emitted organics in addition to those listed in Table 1. This raises the next question, concerned with the reactivity measurement method.

The reactivity measurement method commonly used thus far is the smog chamber method entailing irradiation of the test organic-NO_x mixture and measurement of resultant oxidant yeild. Use of certain kinetic entities (such as rate of organic precursor disappearance or rate constant for the OH-organic reaction) as substitutes for or indices of reactivity has also been proposed (10). In general, the chamber data on oxidant yield are inherently more valid but require extensive and tedious smog chamber tests covering a wide range of reactant organic-to-NO_x ratio conditions. The kinetic indices of reactivity are valid only to degrees depending on their correlation with the oxidant yield data. In the case of the simple, two-class classification scheme proposed here, the most important reactivity data needed are those for the least reactive organics, namely, for the organics comparable to or less reactive than propane. For those organics, the oxidant yield reactivity is extremely difficult to measure reliably because such a measurement is sensitive to interferences from background contamination and organic reagent impurities. Measurements of the rate of organic reactant disappearance and of the rate constant for the OH-organic reaction apparently can be made more reliably (10), but the results do not seem to correlate well with the oxidant yield data, at least, judging from the data in Table 1. Thus, of the 18 organics listed in Table 1, benzaldehyde, benzene, methylene chloride, and acetylene showed rates of organic reactant disappearance that were disproportionately high relative to their oxidant yields (Table 1). It is not known to what degree this inconsistency reflects experimental error or peculiarities in the chemistry of these compounds. Clearly, additional research is needed (a) to establish the relative oxidant-yield reactivities of low-reactivity organics more reliably and for a larger variety of reactant organic-to-NO_x ratio conditions, and (b) to further explore the correlations of oxidant yields with rates of organic precursor reactions and with OH-organic reaction rate constants for a variety of organic compounds, especially halocarbons.

CONCLUSIONS

1. Laboratory evidence continues to provide the only basis for assessing the utility and recommending the use of the reactivity criterion in the oxidant-related control of organic emissions.

2. Occurrence of the pollutant transport phenomenon suggests that the existing reactivity classification of organics be revised to consist of two classes, reactives and unreactives, defined as follows:

- The unreactive organics are those which under optimum irradiation and organic-to-NO_x ratio conditions in an appropriate smog chamber yield no more than 0.08 ppm of O_3.

- Reactive organics are all organics except those found by measurement or theoretical estimation to be unreactive.

Alternatively, if the recent EPA smog chamber data are to be accepted, unreactive organics are defined as those with reactivities lower than the reactivity of propane.

3. Reactivities of unreactive organics are extremely difficult to measure reliably. Uncertainity problems are caused either by experimental error associated with the smog chamber measurement or by the questionable validity of the kinetic indices of reactivity.

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PHOTOCHEMICAL REACTIVITY CLASSIFICATION OF HYDROCARBONS AND OTHER ORGANIC COMPOUNDS

F. F. Farley*

ABSTRACT

A thorough review of oxidant data from smog chamber studies over the past ten years was made by the Western Oil and Gas Association in order to provide the best available basis for a photochemical reactivity classification of volatile hydrocarbons and other organic compounds. Ozone maxima from this review showed reactivity rates varying more than one-hundred fold in a continuous spectrum from methane to the highly reactive 2-methyl-2-butene. These results suggested that a reasonable number of reactivity classes should be selected to cover such a broad range. As was done earlier by Dimitriades and Brunelle, a five-category classification was chosen to provide adequate definition of the broad range of reactivity values observed without over-emphasizing the accuracy of the data. The recent Environmental Protection Agency proposal to classify all volatile organic compounds as either reactive or unreactive does not seem justified; nor does the uneven distribution of compounds and the over-simplification of the three-category classification adopted by the California Air Resources Board. In fact, the "Final Report of the Committee on Photochemical Reactivity to the Air Resources Board" favors a "5-tiered scheme." Pitts has also proposed a five-class reactivity scale based upon five orders of magnitude in hydroxyl radical reaction rates. A five-category reactivity classification would allow feasible substitution of less reactive for more reactive volatile organic compounds, e.g., in surface-coating solvents. Such substitutions are almost precluded by either the proposed two-category reactive-unreactive classification or the California three-category classification.

While some smog chamber studies indicate moderate reactivity for light paraffinic hydrocarbons, three airborne studies indicate very low reactivities. Caution should be exercised in assigning moderate or high reactivities to paraffinic hydrocarbons until further work clarifies these divergent results.

INTRODUCTION

It is well known that hydrocarbon (HC) and other organic compounds contribute to the formation of photochemical oxidants in the atmosphere. The formation of photochemical oxidants takes place at different rates, depending upon the nature and composition of the reactants and upon the ambient conditions existing in the atmosphere. Smog chamber studies designed to determine the reactivity of the various hydrocarbon and organic compounds in simulated atmospheres clearly demonstrate that an extremely wide range in reaction rates and

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product yields exists. A more or less continuous spectrum of rates and yields have been found, ranging all the way from methane, with its extremely low rate of reaction, to highly reactive species such as 2-methyl-2-butene. It seems reasonable, therefore, to classify hydrocarbons and other organic compounds for regulatory purposes according to their rates of photochemical reaction, or more appropriately, according to their ozone (O_3)-forming potential.

When smog chamber data are extrapolated to the real atmosphere, consideration should be given to results obtained from atmospheric reactivity studies such as recent airborne measurements.

The Western Oil and Gas Association (WOGA) review was directed primarily toward reactivity in the traditional sense. This assumes that the photochemical reaction rates and oxidant yields in one solar day's irradiation are of prime importance in judging the impact of a given organic compound on air quality. We recognize the importance of considering this question in a broader sense in light of the recent findings related to oxidant and oxidant precursor transport, high rural oxidant, etc. One theory put forward to explain high rural oxidant points to the slower reacting compounds, unreacted during the first solar day, as being the primary precursors during the next solar day. While we agree that this is a possible explanation, we know of no data which directly show that the slower reacting compounds are the prime source of the O_3, and not the many other compounds present in the air mass, such as organic reaction products of the faster reacting compounds. If the slower reacting compounds are significant precursors, this would tend to diminish the utility of a reactivity scale based on O_3 formation in smog chamber studies for situations where multi-day irradiations could lead to elevated oxidant downwind of an urban area.

SMOG CHAMBER DATA

To determine reactivity classes, all available O_3 maximum concentration data collected in smog chamber studies over the past ten years were pooled. The data, shown in Tables 1 and 2, are normalized to toluene = 1. In the case of data from Gulf, where toluene data were not available, the average propylene value from the other labs reporting propylene was used in the normalization.

These chamber studies, for the most part, involved the irradiation of pure compounds in the presence of nitrogen oxides (NO_x) at a molar HC-to-NO_x ratio (HC/NO_x) of about 2. This ratio is a reasonable approximation to that found in urban atmospheres. For example, studies carried out by Kopczynski, et al. (8) in Los Angeles in 1968 showed an average molar HC-to-NO_x ratio of 2.0. Data presented in a California Air Resources Board (ARB) staff report (9) dated November 13, 1974 substantiate this value. In this report, average 6-9 a.m. measured values for reactive hydrocarbons and total NO_x are given for 1965 to 1972, and projected values are given up to 1985. Allowing for the non-methane hydrocarbons not included in this reactive hydrocarbon tabulation gives a ppm C-to-NO_x ratio of about 8-10, which again, gives a molar ratio of about 2 since the average carbon number of non-methane hydrocarbons in urban atmospheres is about 4.5.

On a day-to-day basis, HC-to-NO_x ratio does vary considerably from the average, and values from 1 to 4 could be expected. The implications of this HC-to-NO_x ratio effect are discussed in more detail later.

TABLE 1. HYDROCARBONS - MAXIMUM OZONE FOR VARIOUS LABORATORIES AT HC/NO_x = 2, NORMALIZED TO TOLUENE = 1

	Laboratory*							
	1	2	3	4	4a	5	6	Avg.
Ethane					0.0			0.0
Propane					0.0			0.0
n-Butene	0.08	0.03	---	0.53	0.03	---	0.0	0.13
n-Pentane			0.95					0.95
i-Pentane					0.33			0.33
n-Hexane	0.10			0.57	0.47			0.33
Cyclohexane						0.59		0.59
n-Octane			0.85	0.63		0.41		0.63
i-Octane	0.13		1.1					0.62
Benzene	0.0		0.20	0.17		0.0		0.09
Toluene	1.0(0.36)**		1.0(0.13)	1.0(0.30)		1.0(0.44)		1.0
Ethylbenzene	0.92		1.0	0.70		0.91		0.88
n-Propylbenzene				0.70				0.70
i-Propylbenzene	0.79			0.63		0.91		0.78
n-Butylbenzene			1.2	0.80				1.00
t-Amylbenzene			0.55					0.55
i-Butylbenzene				0.57				0.57
t-Butylbenzene			0.55	0.43				0.49
o-Xylene	1.5		1.5	1.1		1.0		1.3
m-Xylene			1.7	1.3				1.5
p-Xylene	1.4			0.87				1.1
1,3,5-Trimethylbenzene	1.7		3.2	1.5		1.5		2.0

(continued)

TABLE 1. (continued)

	Laboratory*							
	1	2	3	4	4a	5	6	Avg.
Ethylene	1.6			0.93		1.3		1.3
Propylene	2.0	2.1	1.9	1.8				2.0
i-Butene	1.9			1.6				1.8
i-Hexene	1.7			1.4				1.6
t-2-Butene	2.0			1.5		1.5		1.7
c-2-Butene	2.1			1.5				1.8
2-Me-2-Butene	2.1		3.1	1.6				2.3
2-Hexene	1.7							1.7
Tetramethylethylene				2.0				2.0
1,3-Butadiene	3.2			1.6				2.4

* Laboratory Code (Literature Reference

1. Bureau of Mines (1)
2. Gulf (2)
3. Shell (3)
4. General Motors (4)
4a. General Motors (5)
5. Pattelle (6)
6. EPA (7,14)

** Figures in parentheses are actual max. ozone values for toluene in ppm.

TABLE 2. OXYGENATED COMPOUNDS - MAX. OZONE FOR VARIOUS LABORATORIES AT $HC/NO_x=2$, NORMALIZED TO TOLUENE = 1

	Laboratory*				
	1	2	3	4	Average
Acetone	0	-	0.07	0.1	0.08
Cyclopentanone	-	-	0.55	-	0.55
Cyclohexanone	0.2	0.5	0.6	0	0.42
Methyl ethyl ketone	0.6	0.9	0.9	0.5-1.5	0.8
Diethyl ketone	-	-	1.05	-	1.05
Methyl isobutyl ketone	1.0	0.9	1.35	1.8	1.26
Methyl n-butyl ketone	0.8	-	1.45	-	1.13
Methyl n-propyl ketone	0.5	-	-	-	0.5
Methyl t-butyl ketone	1.4	-	-	-	1.4
Methyl isoamyl ketone	-	1.0	-	-	1.0
Di-n-propyl ketone	0.7	-	-	-	0.7
Di-isobutyl ketone	1.8	-	-	-	1.8
Mesityl oxide	1.5	-	-	-	1.5
Isophorone	1.7	-	-	-	1.7
t-Butyl alcohol	-	-	0.3	-	0.3
Isopropyl alcohol	0.2	1.2**	0.65	-	0.68
Ethyl alcohol	-	-	1.0	1.1	1.05
n-Butyl alcohol	-	-	1.25	-	1.25
Isobutyl alcohol	-	-	1.25	-	1.25
8-Butyl alcohol	-	1.1	1.4	-	1.2
4-Methyl-2-pentanol	-	-	1.45	-	1.4

(continued)

TABLE 2. (continued)

	Laboratory*				
	1	2	3	4	Average
t-Butyl acetate	-	-	0.5	-	0.5
Ethyl acetate	-	0.7	0.8	-	0.75
Isopropyl acetate	-	-	0.85	-	0.85
n-Butyl acetate	-	0.7	0.85	-	0.8
Isobutyl acetate	0.2	1.3	1.0	-	0.8
Sec butyl acetate	-	1.4	-	-	1.4
Phenyl acetate	0	-	-	-	0
Cellosolve acetate	-	1.1	-	-	1.1
Methyl benzoate	0	-	-	-	0
Dimethyl formamide	-	-	0.2	-	0.2
N-Dimethylacetamide	-	-	0.95	-	0.95
Diethyl amine	0.2	-	-	-	0.2
Triethyl amine	0.1	-	-	-	0.1
n-Methyl pyrrolidone	0.7	-	-	-	0.7
Tetrahydrofuran	1.9	-	1.45	-	1.7
Diethyl ether	-	-	2.5	-	2.5

Laboratory Code (Literature reference)
1 - Batelle (6, 13)
2 - SRI (11)
3 - Shell (3)
4 - LAAPCD (10, 15)

** The SRI value for isopropyl alcohol seems to be out of line. Other data from the SRI chamber have also been questioned because of operating difficulties and variations in nitrogen oxide concentrations.

Convenient summary of solvent reactivity data found in Reference 12.

The average normalized values found for each organic compound in the various smog chamber studies are plotted in Figures 1 and 2. Averaging the data is not without some drawbacks, since systematic chamber-to-chamber differences still appear to a certain extent, even after normalization. As a result, the values shown in the "average" column in Tables 1 and 2 for compounds which have been tested in only one or two facilities may reflect a bias peculiar to the facility in question. However, apart from a few compounds, for example, n-pentane, and i-octane, methyl-n-butyl ketone, and isopropyl alcohol, which may be out of line, the data should provide a reasonable estimate of relative reactivity.

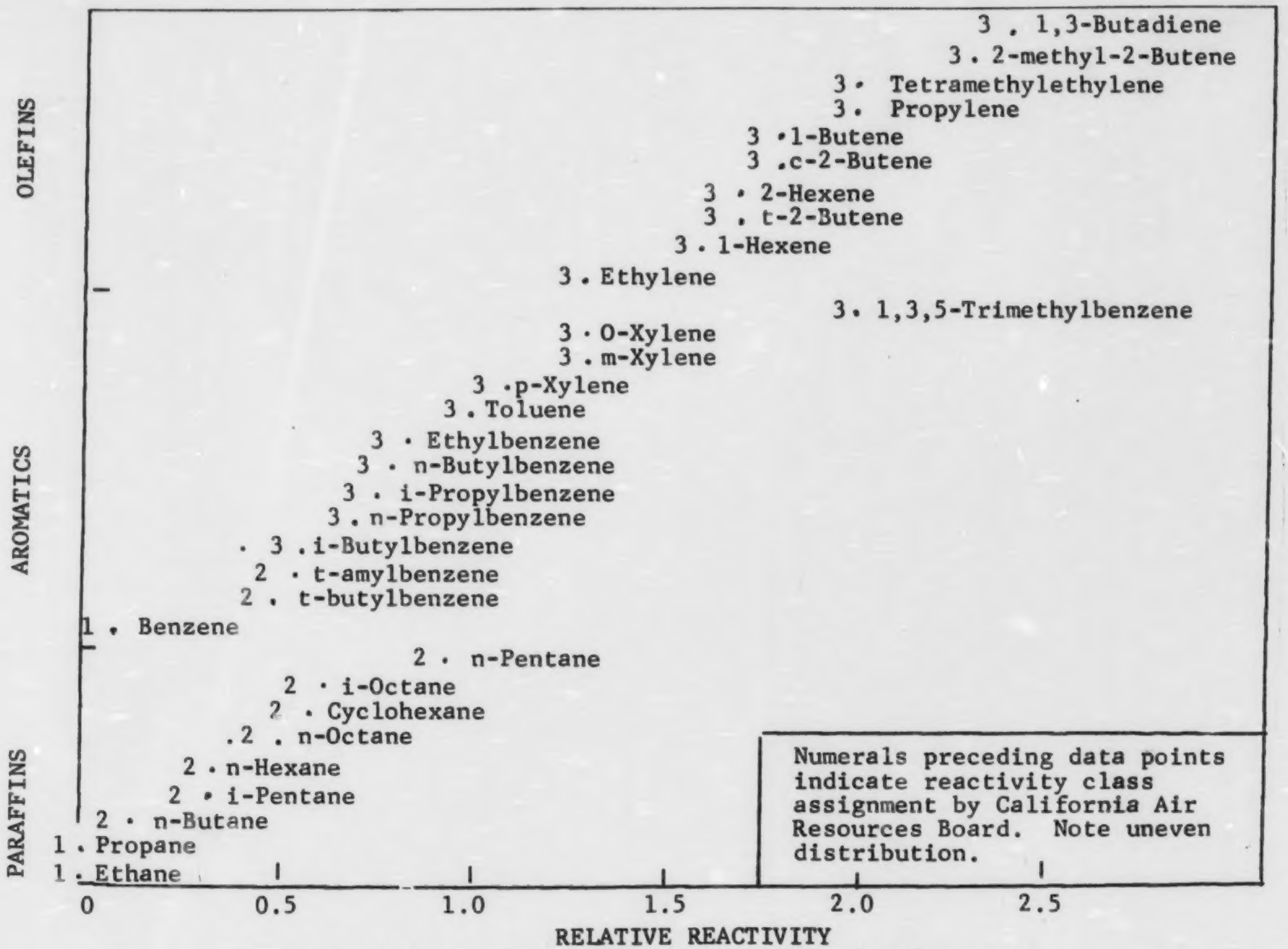
REACTIVITY CLASSIFICATION

In Figure 1, the hydrocarbons are plotted according to class: paraffins, aromatics, and olefins. Generally speaking, the paraffins show the lowest potential for O_3 formation, aromatics show intermediate O_3-forming potential, and the olefins show the greatest potential. The oxygenated solvents are also plotted in Figure 2 according to class: ketones, alcohols, acetates, and miscellaneous. Within the classes, there are some definite trends in reactivity which appear to be structurally related. Based on the data in Figures 1 and 2, and following structural guidelines, the reactivity classes shown in Table 3 were defined.

The data in Tables 1 and 2 and in Figures 1 and 2 show a wide range of photochemical reactivity, over one-hundred fold. This wide range of reactivity covering a more or less continuous spectrum of rates, ranging from methane to highly reactive olefins, suggests that a reasonable number of reactivity classes should be selected to cover such a broad range. The WOGA approach was to define five classes as was done earlier by Dimitriades (12) and others (24). The five-category classification represents a technically sound approach and provides adequate definition of the broad range of reactivity values observed, but at the same time it does not over-emphasize the accuracy of the data by attempting to subdivide further. A five-category classification avoids the uneven distribution of compounds and the oversimplification of the three-category classification recently adopted by the ARB (21). In fact, the "Final Report of the Committee on Photochemical Reactivity to the Air Resources Board" (22), issued after ARB adopted a three-category classification, favors a "5-tiered scheme with an additional sixth or zero class." Pitts, et al. (23) also proposed a five-class reactivity scale based on hydrocarbon disappearance rates due to reaction with hydroxyl radical (OH). They "found it convenient and useful... to employ the order of magnitude divisions which lead to a five-class scale."

As noted in Table 3, the assignment for C_4 paraffins is somewhat uncertain. The data in Table 1 for n-butane at $HC/NO_x = 2$ show very low maximum O_3 values for four separate studies, with a significant value found in only one study. At higher HC-to-NO_x ratio, greater O_3 yields have been observed as is discussed later.

A statistical T test was applied to the data to determine if the difference in means between adjacent categories was significant at the 95% confidence level. The lack of a significant difference would indicate that there is no



Numerals preceding data points indicate reactivity class assignment by California Air Resources Board. Note uneven distribution.

Figure 1. Maximum ozone at $HC/NO_x = 2$, normalized to toluene = 1.

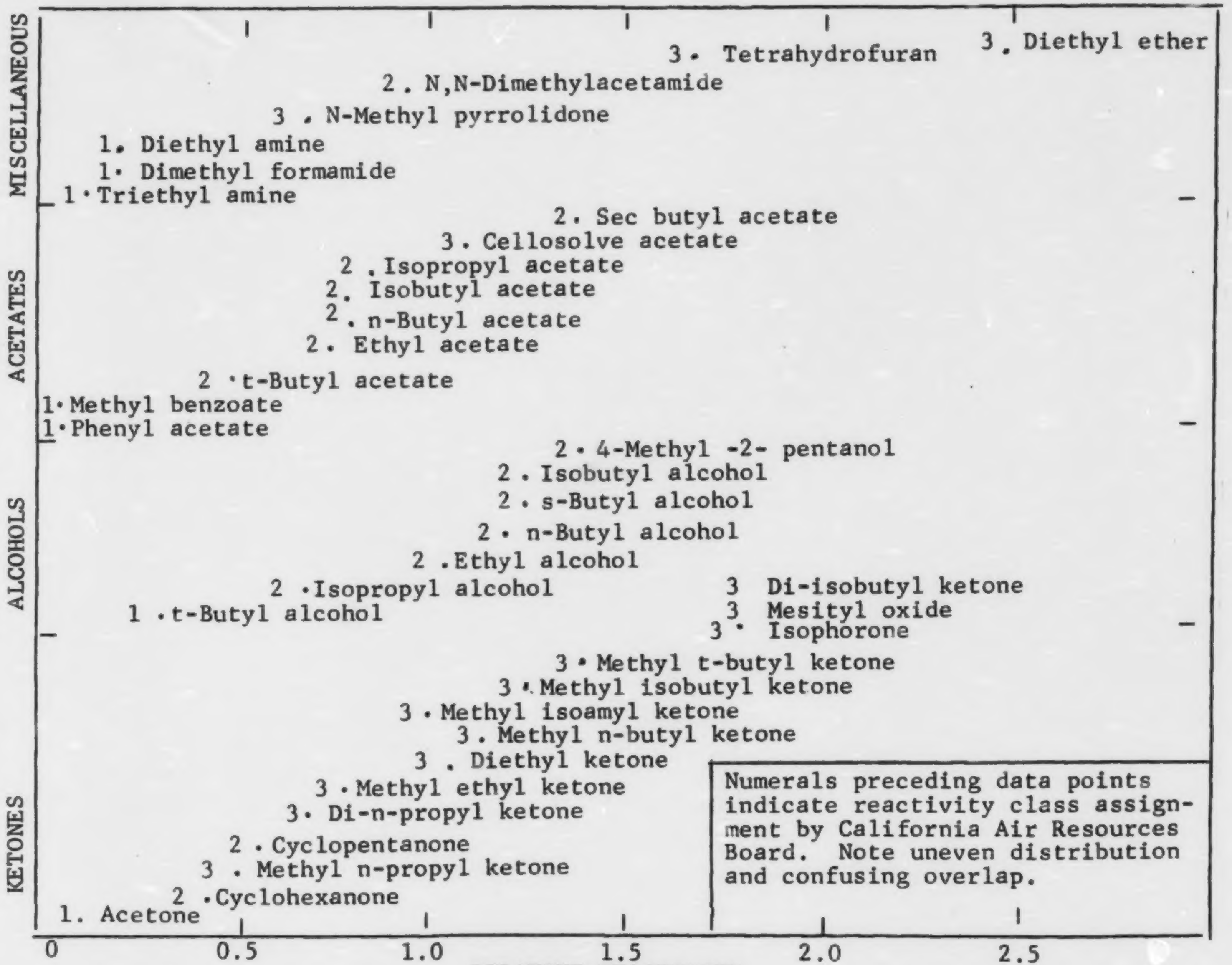


Figure 2. Maximum ozone at HC/NO_x = 2, normalized to toluene = 1.

TABLE 3. REACTIVITY CLASSIFICATION OF ORGANIC COMPOUNDS

Class I	Class II	Class III	Class IV	Class V
Negligible Reactivity	Low Reactivity	Moderate Reactivity	High Reactivity	Very High Reactivity
	Factor = 0.25	Factor = 0.50	Factor = 0.75	Factor = 1.0
C_1 to C_4* Paraffins Acetylene Benzene Acetone Tertiary alkyl alcohols Dimethyl formamide Diethyl amine Triethylamine Methyl benzoate Phenyl acetate	C_5+ Paraffins Tertiary alkyl benzenes Saturated cyclic ketones n-Alkyl ketones Primary alkyl acetates Secondary alkyl acetates Tertiary alkyl acetates N-Methyl pyrrolidone Isopropyl alcohol	Monoalkylbenzenes (except tertiary) Primary alkyl alcohols (except isopropyl) Secondary alkyl alcohols Branched alkyl ketones Dimethyl acetamide Cellosolve acetate	Ethylene Dialkylbenzenes Tetrahydrofuran	Olefins, except ethylene Diolefins Tri- and Tetraalkyl benzenes Diethyl ether

* The scientific evidence now available for the placement of butanes shows a range of reactivity between Class I and II (See Table 1).

justification for making such a separation. This test, which was carried out on the complete data set and not just on the average values, included any lab-to-lab variability in the analysis and showed that the difference in means was significant at a confidence level greater than 95%. It should be noted that an initial attempt to separate the diolefin and substituted internal olefin data from the rest of the olefins as a separate group did not yield a mean which was significantly different from the mean of the rest of the olefins.

As mentioned previously, the data in Tables 1 and 2 and Figures 1 and 2 were essentially all obtained at or near molar HC/NO_x = 2. At lower HC-to-NO_x ratios, O_3 formation is inhibited due to the reaction of O_3 with nitric oxide (NO). At higher HC-to-NO_x ratios, relative reactivities of the more reactive compounds do not seem to be markedly affected. However, chamber studies indicate that the less reactive compounds, such as low molecular weight paraffins, can become more important contributors to O_3 formation (5, 7). The available data for lower molecular weight paraffins at higher HC-to-NO_x were reviewed to determine to what extent they might contribute to O_3 formation on days when HC-to-NO_x was greater than the average. The relevant data are shown in Table 4.

TABLE 4. REACTIVITY OF PARAFFINS AS A FUNCTION OF HC/NO_x

Compound	Max. Ozone for Various Laboratories*								
	2			4a			6		
Molar HC/NO_x =	2	4	6	2	4	6	2	4	6
PPM HC/NO_x =	8	16	24	8	16	24	8	16	24
Ethane	-	-	-	0.0	0.0	0.3	-	-	-
Propane	-	-	-	0.0	0.13	0.40	-	-	-
n-Butane	0.03	0.41	-	0.03	0.60	0.77	0.0	0.0	0.0
i-Pentane	-	-	-	0.33	1.03	1.00	-	-	-
n-Hexane	-	-	-	0.47	1.00	0.93	-	-	-

* Values normalized as in Table 1.

The most complete data set is contained in a study by Heuss (5). This shows a definite trend to higher O_3 potential for n-butane, i-pentane, and n-hexane at HC-to-NO_x of 4 and 6, compared to the values at 2. The Gulf study shows a similar trend for n-butane (2). However, the work by Altshuller, et al. (7) shows essentially no O_3 formation from n-butane until the HC-to-NO_x reaches about 10. Overall, the data suggest that under typical ambient conditions, as exemplified by HC-to-NO_x of 2, the C_1-C_4 paraffins are properly categorized in Class I and the C_5+ paraffins in Class II. While at the higher HC-to-NO_x there is evidence of increased reactivity for the C_{5+} paraffins, this does not appear to be sufficient cause for removal of the C_{5+} paraffins from the Class II category in the general purpose scale.

ATMOSPHERIC REACTIVITY STUDIES

Three airborne studies have been conducted recently that indicate low photochemical reactivity for light paraffinic hydrocarbons. These studies are the refinery plume study of Westberg and Rasmussen (16), the Portland plume study of Londergan and Polgar (17), and and analysis of LARPP (Los Angeles Reactive Pollutants Projects) data by Calvert (18, 19, 20). Further experimental work is needed to verify the low reactivities for light paraffinic hydrocarbons found in these airborne studies, and caution should be exercised in assigning moderate or high reactivities to paraffinic hydrocarbons on the basis of smog chamber experiments alone.

CONCLUSIONS

A review of all available O_3 data from smog chamber studies has been used to prepare a photochemical reactivity classification of hydrocarbons and organic compounds. This review was confined to O_3 (oxidant) formation to provide the broadest scientific base for a reactivity classification. The very wide range of photochemical reactivities encountered in this and other reviews argues for a multi-class scale, such as the five-class scale proposed herein. A five-category classification provides adequate definition of the broad range of reactivity values observed and does not over-emphasize the accuracy of the data.

The significance of recent airborne measurements of photochemical reactivity of light paraffinic hydrocarbons should be given careful consideration.

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SESSION 15

ATMOSPHERIC CHEMISTRY AND PHYSICS

Chairman: J.G. Calvert
Ohio State University

DECOMPOSITION OF CHLORINATED HYDROCARBONS UNDER SIMULATED ATMOSPHERIC CONDITIONS

F. Korte and H. Parlar*

ABSTRACT

This paper deals with industrial organic chemicals which are not generally classified as air pollutants although they are also present in air. The fate of the persistent industrial chemicals, e.g. chlorinated substances like PCB's, DDT, HCB, Pentachlorphenol, or the so-called chlorinated hydrocarbon pesticides under atmospheric conditions are discussed. From model calculations with DDT it is known that the concentrations actually found in the environment are considerably lower than calculated. On the basis of production figures, there must exist a non-identified sink in the environment. In experiments under simulated atmospheric conditions, the mineralization of such persistent substances as pentachlorphenol, dieldrin and others can be demonstrated. Thus, atmospheric mineralization might be the final sink for many other chemicals which are exposed to sunlight either after evaporation or on the solid earth's surface. The kinetics of breakdown to carbon dioxide and hydrochloric acid is presented for several model chemicals.

INTRODUCTION

Problems caused by environmental chemicals have a wide range of chemical, biological and meteorological aspects. This report focuses mainly on the chemical aspects.

Environmental chemicals are introduced into the air in several ways: through air transport, from aeroplane application, by evaporation from plants and soil and via transpiration by plants. For instance, four weeks after foliar application of 1.2 mg of ^{14}C-labelled endrine per plant on white cabbage, residues in plants and soil amounted only to six per cent; 94 per cent had disappeared into the atmosphere.

In the atmosphere, environmental chemicals can be converted through photochemical reactions. The ratio between the particle form and the free molecular gaseous form is not known. It is difficult to determine the exact form in which the molecules are found in the various atmospheric layers, since they can exist either as single molecules, as clusters, or can be adsorbed to aerosols. For this reason development of a model to simulate

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atmospheric conditions is advised.

What chemical changes do environmental chemicals undergo after they are released into the atmosphere? Because of the difficulties involved in direct atmospheric studies, experiments in the laboratory is the approach that allows for conclusions to be derived on the behaviour of a chemical in the environment. Photochemical experiments under simulated atmospheric conditions lead to an understanding of the relative reactivities of environmental chemicals, and of the formation pathway and identities of photoproducts -- the latter usually occurring at low concentrations. Photochemical reactions in solution simulate conversion of these compounds when dissolved in plants waxes.

RESULTS AND DISCUSSION

Since 1968, the authors have been studying the behaviour of cyclodiene insecticides under simulated atmospheric conditions. It is known that these substances exist in the atmosphere, on the surface of plants and in soil, and that under these conditions UV-irradiation may lead to structural conformations. The purpose of the study reported here was to investigate the mechanisms by which compounds like aldrin, dieldrin and photodieldrin--chosen as model substances--chemically change under simulated atmospheric conditions, and to identify the products resulting from such changes. Various photoreaction types of cyclodiene insecticides are known (1). Two of these reactions are shown in Figures 1a and 1b.

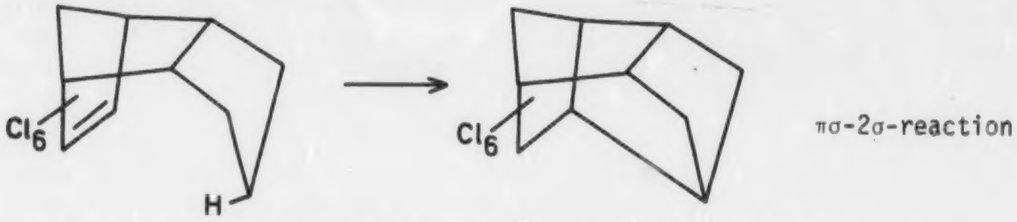


Figure 1(a). The $\pi\sigma$-2σ reaction of cyclodiene insecticides.

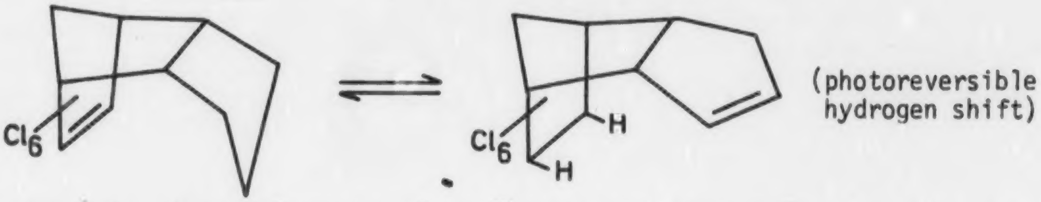


Figure 1(b). The photoreversible hydrogen shift of cyclodiene insecticides.

The $\pi\sigma$-2σ-reaction: The cyclodiene insecticides contain a chlorinated double bond, which can be excited by long-wave UV-light (300 nm). By interaction with the methylene bridge in the non-chlorinated part of the molecule, the corresponding photoisomeric product can be formed by a $\pi\sigma$-2σ-reaction. The excited double bond abstracts the opposite H-atom, whereby a new 2σ-bond is formed.

The photoreversible hydrogen shift: It could be shown that, during sensitized irradiation of chlordane derivatives, intramolecular reversible hydrogen shifts are possible as well as the $\pi\sigma$-2σ-reactions typical for this class of substances. Irradiation of chlordane derivatives at low temperatures showed that below -30°C, the hydrogen transfer isomers are the only photoproducts. The parent compounds are obtained also by irradiation of hydrogen transfer isomers.

Dechlorination reaction: In protonated solvents as well as in the solid phase, cyclodiene insecticides are photochemically dechlorinated at the chlorinated double bond. It may be assumed that the dechlorination reactions proceed from the singlet state of the molecule.

Reactions with reactive oxidizing agents: It is known that cyclodiene insecticides in the atmosphere are found after their application (gaseous or adsorbed to aerosols). These substances change their light absorption characteristics under adsorbed conditions; for instance, the adsorption maximum of photodieldrin (195 nm in hexane) under adsorbed conditions on silicon dioxide (SiO_2) moves to longer wavelengths (260 nm). This adsorption shift reveals that even photodieldrin in an adsorbed form can be excited by wavelengths even higher than 260 nm, so that a possible reaction under the photochemical conditions of the lower atmosphere (with wavelength $\lambda > 290$ nm) cannot be excluded.

Photoreactions in the atmosphere further depend on altitude (because of the increasing radiation intensity of the short-wave UV-irradiation at higher altitudes and the presence of other reactive substances). Due to the vast number of possible reactions in the atmosphere and the lack of experimental information, at the present time it is impossible to estimate the rates of the individual steps.

Table 1 shows a compendium of photoreactions of aldrin (2).

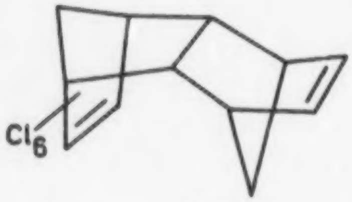
Non-sensitized irradiation of solvents of dieldrin (protonated solvents) with wavelengths above 290 nm yielded mainly dechlorination products. On the other hand, the isomeric product was found in sensitized reaction. From the photochemical standpoint dieldrin is inert in comparison to aldrin, and dechlorination and isomerization reactions proceed more slowly.

Nitrogen dioxide (NO_2) is a prominent inorganic air pollutant because of its generation resulting from combustion of fossil fuels. Its possible role, therefore, in atmospheric photochemistry of chlorinated hydrocarbons should be considered.

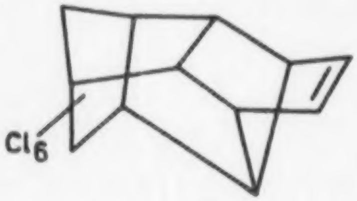
The compounds in Figure 2 were isolated from solutions of dieldrin and nitrogen tetroxide in fluorocarbon after irradiation with UV-light having long wavelengths ($\lambda > 300$ nm) (3). Irradiation of dieldrin and nitrogen tetroxide in carbon tetrachloride under similar conditions yielded the same compounds. The OH-compounds were detected after irradiation of a solution of dieldrin and ozone (O_3) in fluorocarbon. In the presence of NO_2, dieldrin distributed in nitrogen in the gaseous state was converted mainly into photodieldrin by UV-light. Irradiation of dieldrin gaseously distributed in ozonized air yielded, as in ozonic solution, several products of higher molecular weight, which, however, were not isolated.

TABLE 1. PHOTOREACTIONS OF ALDRIN

Phase	Time of irradiation	Type of lamp	Wavelength nm	Conversion	Photoproducts (Yield)
Film on glass	2 hrs.	HPK 125	290	74	I (41) II (5) III (2) V (1) Polymer (not identified) (25)
Film on glass	1 month	Sunlight	290	97	I (24) II (4) III (9) Polymer (60)
Adsorbed on SiO_2	16 hrs.	HPK 125	290	84	I (4) II (55) III (2) IV (4)



Aldrin



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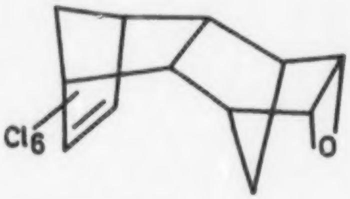

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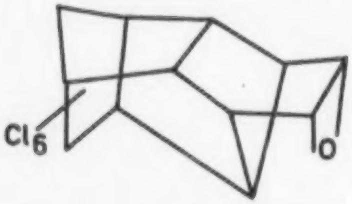

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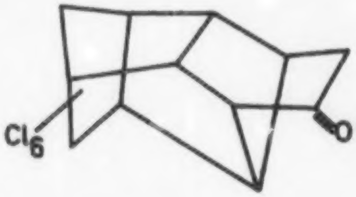

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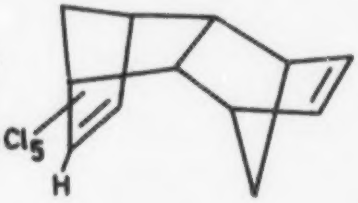

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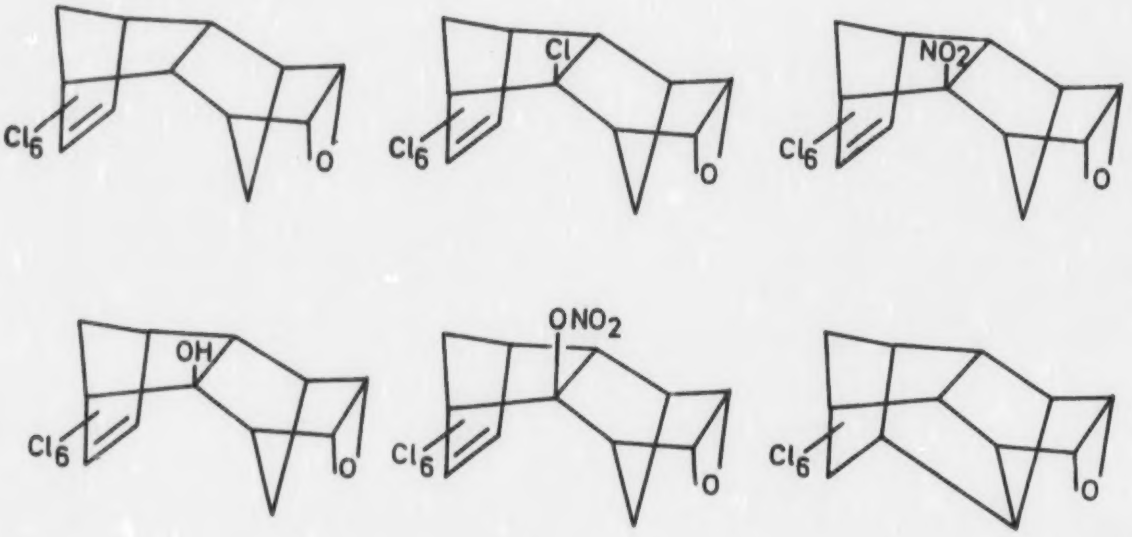

Figure 2. Photochemical reactions of Dieldrin in the presence of NO_2.

During irradiation of dieldrin in solution, adsorbed or in the gas phase, photodieldrin is produced. Dieldrin was chosen for irradiation in order to determine the conditions which cause a complete decomposition (mineralization) because it is considered to be one of the most persistent chemicals.

Tests in the gas phase, however, revealed that isomeric photodieldrin is produced in large yield. This can be explained by a much longer life time of the electronically excited state of the dieldrin molecule in the gas phase. These conditions produce a large yield for compounds formed by the more favorable bridging reaction in comparison to the bimolecular reactions with oxygen species. In presence of O_3 a hydroxy product has been formed in smaller quantities. Irradiation of adsorbed dieldrin in an oxygen stream at wavelengths below 300 nm revealed that dieldrin is almost quantitatively degradated to carbon dioxide (CO_2) and hydrochloric acid (HCl). Small amounts of photodieldrin were found as well. Furthermore, we have found that ethanol and n-hexane also, adsorbed on silica gel, undergo photomineralization with wavelength above 300 nm to give CO_2.

In addition to our investigation with cyclodiene insecticides, we have investigated the behaviour of hexachlorobenzene, pentachlorobenzene, pentachlorophenol, 1,1,1-trichloro-2, 2-bis (p-chlorophenyl)ethane (DDT), 1,1-dichloro-2, 2-bis(p. chlorophenyl)ethylene (DDE), 2,4,5,2',4',5'-hexachlorobiphenyl and 2,5,2',5'-tetrachlorobiphenyl in the presence of oxygen with wavelengths 230 nm (quartz glass) as well as with wavelengths 290 nm (pyrex glass) (4). A higher conversion rate was found for substances adsorbed on particulate matter than for substances deposited on a glass surface as solids or as a thin film (see Tables 2 and 3).

TABLE 2. RESULTS OF UV-IRRADIATION OF AROMATIC XENOBIOTICA AS SOLIDS IN AN OXYGEN STREAM

Compound	Irradiation Conditions	Initial Solid Material	Recovered Solid Material	Mineralization Products CO_2	HCl	Cl_2
2,4,5,2',4',5'-Hexachloro-biphenyl	Quartz (7 days)	73 mg	36 mg	53 mg	19 mg	n.d.
	Pyrex (7 days)	70 mg	68 mg	n.d.	n.d.	n.d.
2,5,2',5'-Tetrachloro-biphenyl	Pyrex (7 days)	101 mg	99 mg	n.d.	n.d.	n.d.
Hexachloro-benzene	Quartz (2 days)	63 mg	23 mg	46 mg	13 mg	13 mg
	Pyrex (7 days)	82 mg	81 mg	n.d.	n.d.	n.d.
Pentachloro-benzene	Pyrex (7 days)	64 mg	62 mg	n.d.	n.d.	n.d.
Pentachloro-phenol	Pyrex (7 days)	80 mg	69 mg	13 mg	6 mg	n.d.
DDT	Pyrex (7 days)	54 mg	89 mg	12 mg	2 mg	n.d.
DDE	Pyrex (7 days)	98 mg	85 mg	10 mg	8 mg	n.d.

n.d. = not detected

TABLE 3. RESULTS OF UV-IRRADIATION OF AROMATIC XENOBIOTICA ADSORBED ON SILICA GEL

Compound	Initial quantity adsorbed[x]	Quantity remaining adsorbed after 4 days' irradiation[xx]	Quantity remaining adsorbed after 7 days' irradiation[xxx]	Photoproducts detected after 7 days' irradiation[xx][xxx]
Pentachlorophenol	102 mg (100 g)	24 mg (25 g)	12 mg (12 g)	none
DDT	185 mg (100 g)	298 mg (77 g)	255 mg (66 g)	none
DDE	162 mg (100 g)	91 mg (25 g)	69 mg (19 g)	Dichlorobenzophenone 38 mg Trichlorobenzophenone 7 mg

x) In each case the substance was adsorbed on 100 g silica gel

xx) Quantitation was by means of gaschromatography (EDC) and comparison with standard solutions of known concentration as well as by measurements of the UV-extinction.

xxx) The possibility that more polar compounds arise, which are not eluted under these conditions, and consequently are not detected, can not be excluded.

These differences can be attributed to bathochromic shift, i.e., changes in the relative extinction or appearance of new absorption bands as a consequence of the adsorption on silica gel, as well as to the greater dispersion of environmental chemicals/molecules in the adsorbed phase resulting in a higher environmental chemicals/oxygen contact. The disappearance of the reactant substances (see Table 3) cannot be explained by vaporization, nor is it due to the formation of photoproducts. Since CO_2 and HCl are formed during "pyrex"-irradiation of pentachlorophenol, DDT, and DDE as solids on glass (see Table 2) and also the UV-absorption bands of these compounds are located nearly in the same region as those of the substances adsorbed on silica gel, we deduce that this is a case of mineralization.

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PHOTOOXIDATION OF THE TOLUENE-NO_2-O_2-N_2 SYSTEM IN A SMALL SMOG CHAMBER

H. Akimoto, M. Hoshino, G. Inoue, M. Okuda, and N. Washida*

ABSTRACT

Photooxidation of the toluene-NO_2-O_2-N_2 system has been studied in a 67-liter smog chamber, with radiation provided by a full arc of a high pressure Xenon lamp through a Pyrex window. Irradiation of air mixtures containing 34 ppm toluene and 10-20 ppm nitrogen dioxide yielded as reaction products benzaldehyde, o-cresol (the m- and p-isomers were less than a few percent of the o-isomer), benzyl nitrate, m-nitrotoluene, and mitrocresols. When nitrous acid was added as a source of additional hydroxyl groups, the m-nitrotoluene yield increased markedly relative to the cresols yields, for the same initial concentration of nitrogen dioxide. Product yields have been studied as functions of reactant concentrations and the reaction mechanism is discussed.

INTRODUCTION

The photooxidation of aromatic hydrocarbons has been the subject of several studies (1-3) in which the aromatic hydrocarbon/NO_2/air reaction system was used as a model of urban atmospheric reaction systems. However, in most of these studies, the emphasis was on the so-called "photochemical reactivity" property of the aromatics; investigations of reaction products characteristic of the aromatic reactant have rarely been carried out.

The purpose of this study is to elucidate the reaction mechanism of the photooxidation of the toluene-NO_2-O_2-N_2 system in the concentration range of 34 ppm of toluene, 10-310 ppm of nitrogen dioxide (NO_2) in nitrogen (N_2) and/or oxygen (O_2) at 1 atm.

EXPERIMENTAL

The reaction chamber was a 1660 x 240 mm (inside diameter) Pyrex tube of 67 liter capacity. It was evacuable to less than 1×10^{-6} torr. Each end of the reaction chamber was sealed with a Pyrex window 20 mm thick, through which a photolyzing light beam was transmitted into the gas sample. The light source was a 500 W xenon short arc lamp, and a parallel light beam of 200 mmϕ was obtained with an elliptical mirror, a lens , and an off-axis parabolic mirror. Figure 1 shows the schematic diagram of the small smog chamber used in the present study.

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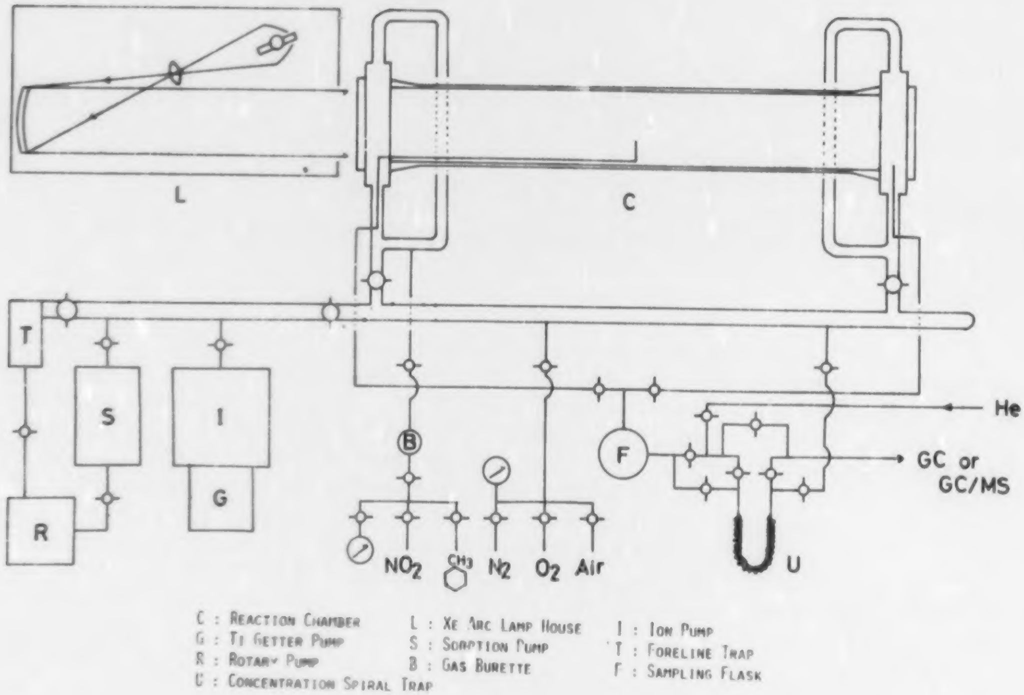


Figure 1. Schematic diagram of the small smog chamber system.

The reaction mixture was first sampled into a constant volume glass sampling bulb (about 700 cc) and then concentrated in a gas chromatograph (GC) sampling tube. The sampling tube was a Pyrex spiral of 2 mm inside diameter and about 4 m extended length. The concentration of the reaction mixture was achieved by evacuating the air and NO_2 while cooling the tube with ethanol-liquid N_2 at -60°C. After the concentration, the sampling tube was heated with hot water and the sample was fed directly into a gas chromatograph. This procedure was found to minimize the thermal reaction of NO_2 with toluene and cresols in the sampling tube.

Product identification was performed with a gas chromatograph mass spectrometer (JEOL, JMS-D100), using a 3 m GC column of SE-30 on Shimalite W. The GC oven temperature was raised from 80°C to 200°C at a rate of 4°C/min. Quantitative GC analysis was carried out using the same column as above.

RESULTS AND DISCUSSION

In the present study, the wavelength of the irradiation light is limited to about 350 nm and longer. In this spectral region, the photooxidation of the toluene-NO_2-O_2-N_2 system is initiated by the photodissociation of NO_2.

$$NO_2 + h\nu \rightarrow NO + O. \qquad (1)$$

The radiation intensity gave a photodissociation rate coefficient for NO_2 of 1.1×10^{-3} sec^{-1}.

Typical GC patterns of the products in the toluene-NO_2-N_2 and toluene-NO_2-air systems are shown in Figure 2. In the reaction system of toluene (34 ppm)-NO_2(11 ~ 207 ppm)-O_2/N_2 (1 atm), benzaldehyde, o-cresol (other isomers are less than a few percent of o-cresol), benzylnitrate, m-nitrotoluene, and nitrocresol (mainly 6-nitro-o-cresol) are formed as reaction products. In the presence of enough O_2, such as in the air atmosphere, oxygen atoms produced in reaction (1) react mainly with O_2 to form ozone (O_3), and in a small fraction of time the remaining oxygen atoms react with toluene. Since O_3 and nitric oxide (NO) react fast enough to regenerate NO_2 dissociated in reaction (1), the concentrations of NO_2 and NO reach their photoequilibrium levels within 20 minutes after the irradiation starts. The photoequilibrium concentration of NO_2 was found to be about half of the initial NO_2 concentration in the air atmosphere, and remained nearly constant during the entire irradiation. Since the NO_2 concentration remains constant, the yield of each product theoretically should increase linearly with irradiation time. This was confirmed experimentally.

The yield ratio of nitrocresol to cresol increases linearly with the equilibrium concentration of NO_2, as shown in Figure 3. But the yield ratio of benzaldehyde to the sum of cresol and nitrocresol was found to be nearly constant and independent of the equilibrium concentration of NO_2, as shown in Figure 4. Because of this independency, the yield of other products was normalized to that of the sum of cresol and nitrocresol. Typical data of the product yield are shown in Table 1.

TABLE 1. RELATIVE PRODUCT YIELDS IN THE PHOTO-OXIDATION OF THE TOLUENE-NO_2-O_2-N_2 SYSTEM AS NORMALIZED TO THE SUM OF CRESOL AND NITROCRESOL

NO_2 (ppm)	HNO_2 (ppm)	Atmosphere (1 atm.)	Benzaldehyde	Benzylnitrate	α-Nitrotoluene	m-Nitrotoluene
180	-	air	0.18	0.057	-	0.025
180	-	N_2	-	-	0.14	0.029
50	-	air	0.17	0.044	-	0.056
50	-	N_2	-	-	0.081	0.039
10	-	air	0.19	0.019	-	0.071
2	15	air	0.47	-	-	0.28

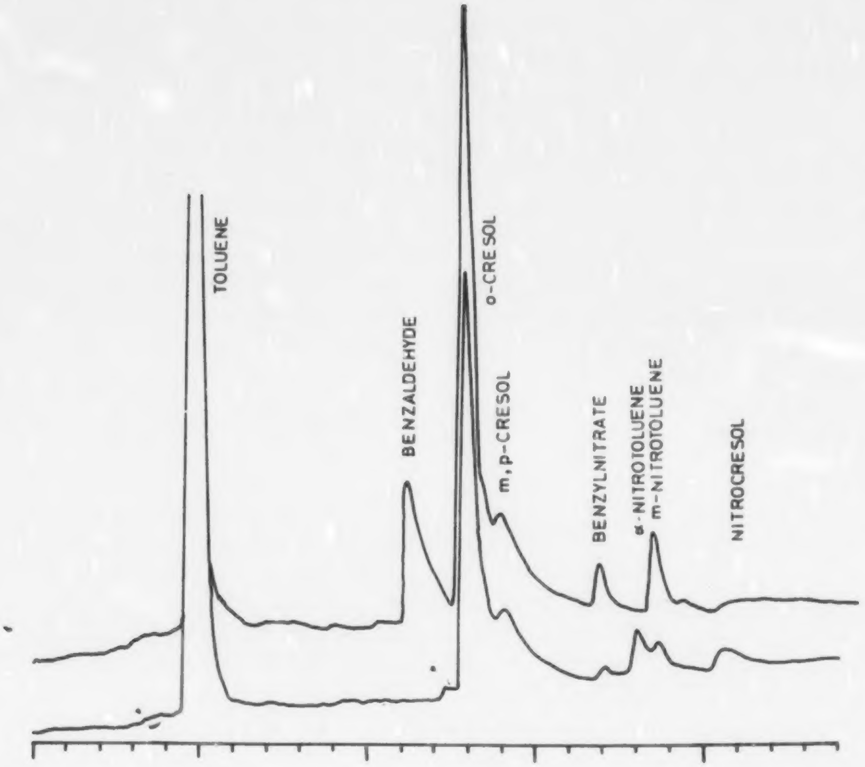


Figure 2. Typical GC pattern of the products: upper curve - toluene 34 ppm, NO_2 54 ppm, air 1 atm; lower curve - toluene 34 ppm, NO_2 54 ppm, N_2 1 atm.

In the reaction system of toluene (34 ppm)-NO_2 (50 ~ 310 ppm)-N_2 (1 atm), α-nitrotoluene is formed in addition to cresol, m-nitrotoluene, and nitrocresol, but the production of benzaldehyde is completely suppressed. The relative yield of α-nitrotoluene to the sum of cresol and nitrocresol increased with the increase of the initial concentration of NO_2, as shown in Figure 5. The production of α-nitrotoluene suggests the presence of the benzyl radical and implies that the hydrogen abstraction from the methyl group of toluene by the oxygen atom does occur. Although Jones and Cvetanovic (4), Grovenstein and Mosher (5), and Gaffney, et al. (6) did not detect any product originating from primary hydrogen abstraction, it is possible that under their experimental conditions, the benzyl radical may not have been chemically trapped.

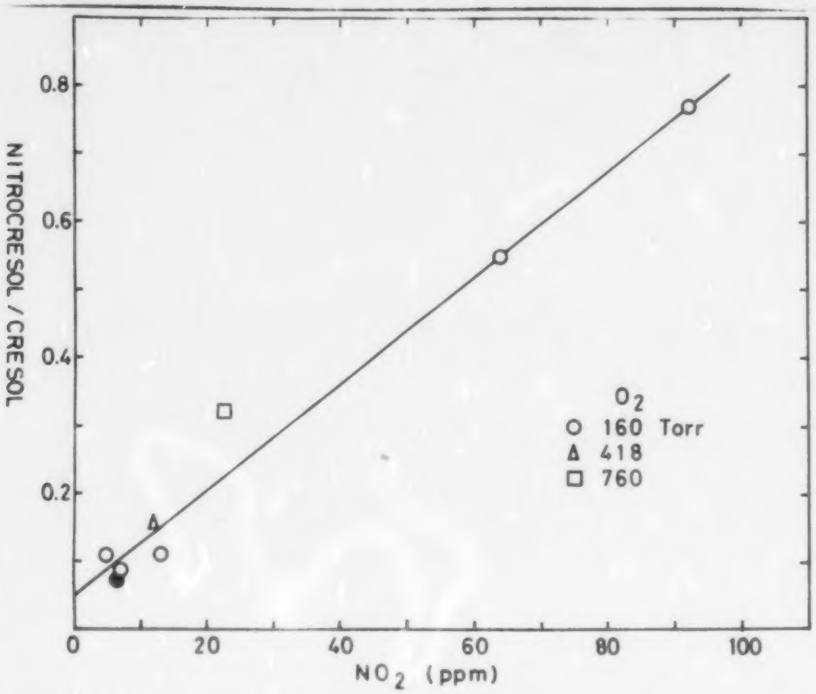
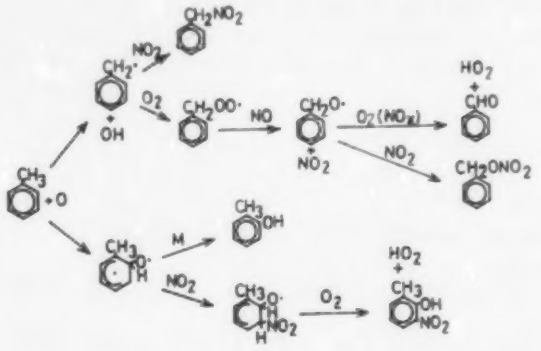


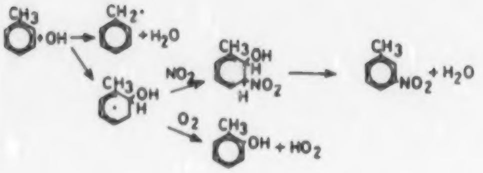
Figure 3. The ratio of nitrocresol to cresol vs. equilibrium concentration of NO_2.

The reaction scheme of the toluene-NO_2-O_2/N_2 system under our experimental conditions may be summarized as:



(2)

In Table 1 it is interesting to note that the relative yield of m-nitrotoluene decrease with the increase of NO_2 concentration both in the O_2-free and O_2-present systems. This is also demonstrated in Figure 6. The formation of m-nitrotoluene would be explained by the reaction initiated by hydroxyl (OH) radical:



(3)

The competition between reaction (3) and the following reactions

$$OH + NO + M \rightarrow HNO_2 + M \quad (4)$$

$$OH + NO_2 + M \rightarrow HNO_3 + M \quad (5)$$

would explain the decrease of the relative yield of m-nitrotoluene at higher NO_2 concentrations. This assumption was supported by experiments on the toluene-HNO_2-NO_x-air system, where OH was formed in the photolysis of nitrous acid (HNO_2).

$$NHO_2 + h\nu \rightarrow NO + OH \quad (6)$$

As shown in the last row of Table 1, in addition to cresol and benzaldehyde, m-nitrotoluene is a main product.

According to the above reaction scheme, the formation ratio of (α-nitrotoluene + benzylnitrate + benzaldehyde) to (cresol + nitrocresol) should be constant in the toluene-NO_2-O_2/N_2 system and is equal to the branching ratio of abstraction to addition in the reaction of oxygen atoms with toluene. Figure 7 shows the ratio in the experiment for various initial concentrations. Thus, the abstraction-to-addition ratio in the reaction of oxygen atoms with toluene is determined to be 0.22 ± 0.02. This value should be considered as the upper limit since the contribution of the OH radical reaction may not be negligible.

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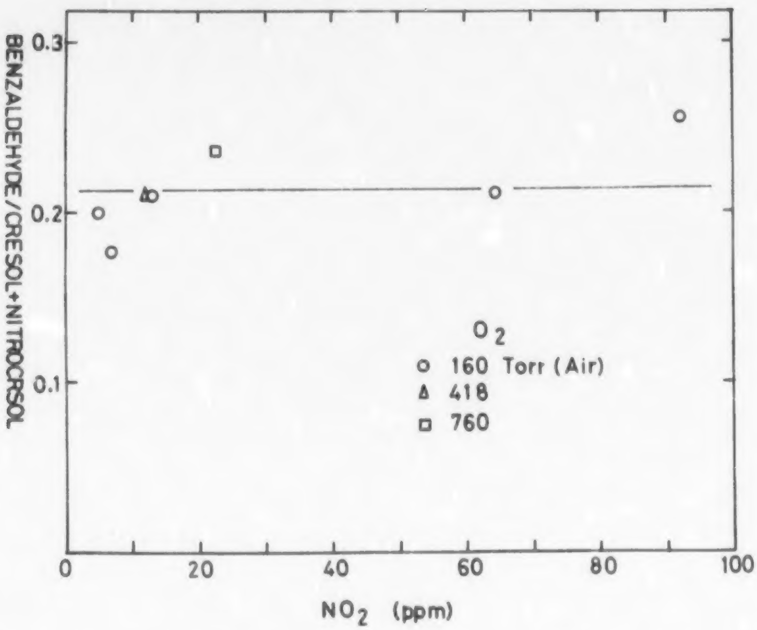

Figure 4. The ratio of benzaldehyde to the sum of cresol and nitrocresol vs. equilibrium concentration of NO_2.

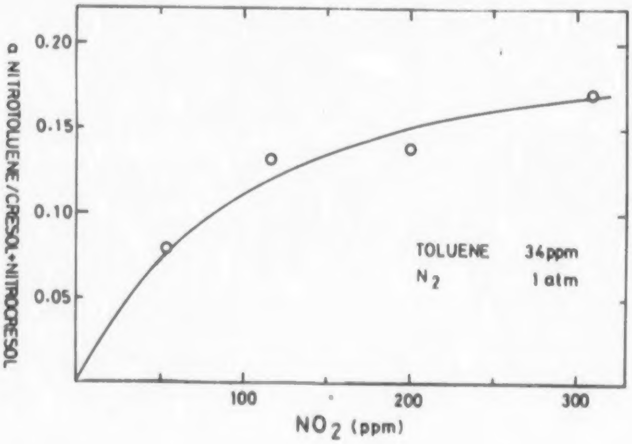

Figure 5. The ratio of α-nitrotoluene to the sum of cresol and nitrocresol vs. initial concentration of NO_2.

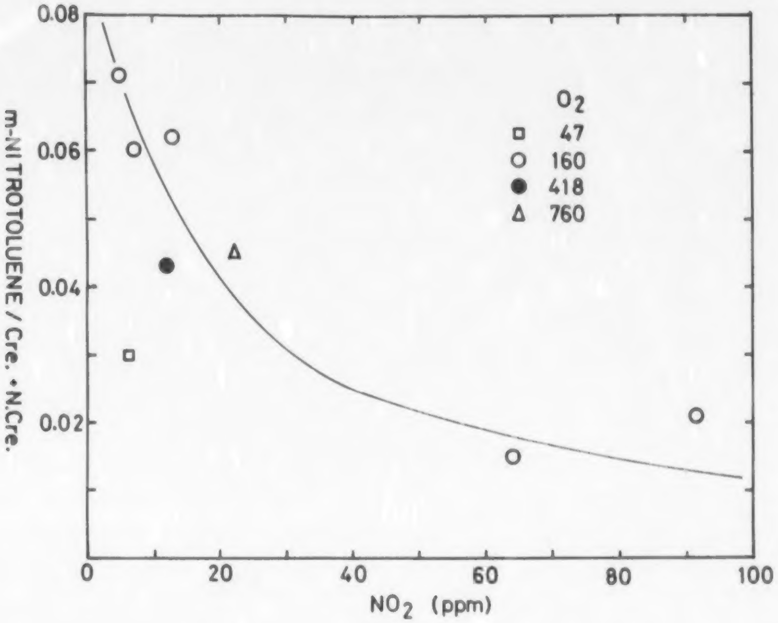

Figure 6. The ratio of m-nitrotoluene to the sum of cresol and nitrocresol vs. equilibrium concentration of NO_2.

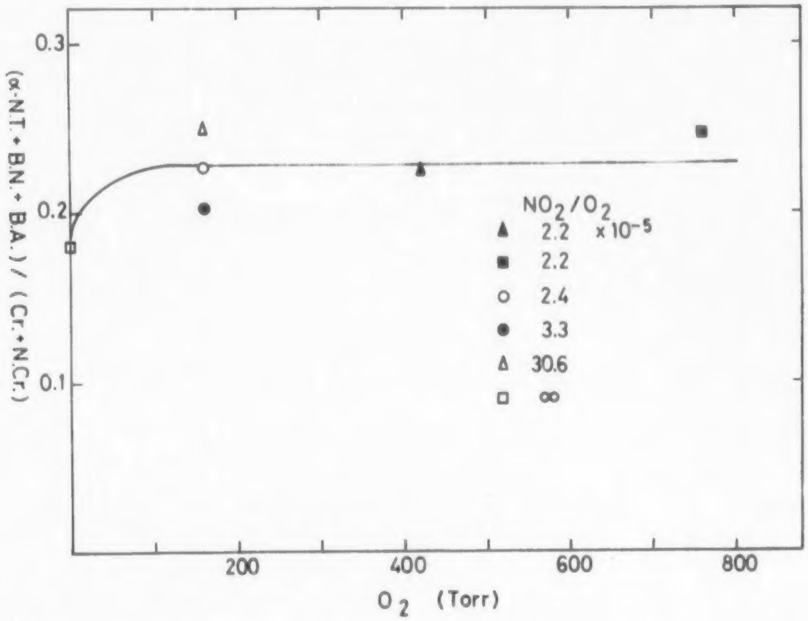

Figure 7. The ratio of (α-nitrotoluene + benzylnitrate + benzaldehyde) to (cresol + nitrocresol) vs. partial pressure of O_2.

THE CHEMISTRY OF NATURALLY EMITTED HYDROCARBONS

B. W. Gay, Jr. and R. R. Arnts*

ABSTRACT

To better understand unusually high rural oxidant concentrations, the chemistry of a number of naturally emitted hydrocarbons, mainly terpenes, was investigated. Photochemical studies were conducted on selected natural hydrocarbons to determine rates of disappearance, ability to produce ozone, and reaction products. Results showed that ozone formation is a function of the initial hydrocarbon-to-nitrogen-oxides ratio, that terpenes react rapidly with ozone, and that gaseous peroxyacetylnitrate is a common terpene reaction product.

INTRODUCTION

The emissions and reactivities of natural compounds have particular significance in understanding unusually high rural oxidant concentrations and a more obvious phenomenon--the aerosol haze characteristic of rural areas like the Smokey Mountains in North Carolina or the Blue Ridge Mountains of Virginia. Natural emissions emitted into the atmosphere by various forms of vegetation include oxygen(O_2), hydrogen(H_2), low molecular weight hydrocarbons (methane, acetylene, ethylene, etc.), high molecular weight hydrocarbons (olefins and aromatics), alcohols, aldehydes, and organic acids. Rasmussen et al., (1) has estimated that the ratio by weight of natural to anthropogenic emissions on a worldwide basis is about 4 for unreactive hydrocarbons (biological processes in swamps being the largest source) and about 6 for reactive hydrocarbons (biological processes in forests) (1). Even though the combined worldwide emissions of natural hydrocarbons (HC) is immense, emissions from individual trees are minute.

The Environmental Protection Agency (EPA) is conducting and supporting laboratory and field studies to provide a data base on natural hydrocarbon emissions, ambient oxidant profiles, hydrocarbon reactivities, and other vital parameters necessary to assess the influence of naturally emitted hydrocarbons on the ambient air quality of rural and urban areas. The photochemistry of C_1-C_4 hydrocarbons and oxygenated hydrocarbons, such as aldehydes, ketones, and acids, has been previously examined with respect to atmospheric chemistry (2,3).

The photochemical research reported in this paper concerns a number of high molecular weight hydrocarbons consisting essentially of terpenes. The main source of emitted terpenes is conifers. Since forests of conifers cover large areas of the world, terpenes possibly could play an important role in the formation of rural oxidants.

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The natural hydrocarbons selected for study were isoprene, myrcene, α-and β-pinene, p-cymene, Δ-carene, d-limonene, and terpinolene. All of these hydrocarbons, except isoprene, are terpenes. Furthermore, they have been identified in the atmospheres of loblolly forests during field studies. To assess rates of disappearance, ability to produce ozone, and reaction products, each hydrocarbon was exposed to simulated ultraviolet (UV) light in the presence of nitrogen oxides (NO_x). The formation of ozone (O_3) and other gaseous products was monitored by a variety of analytical methods.

EXPERIMENTAL

SMOG CHAMBER STUDIES

Smog-chamber-type irradiations of the natural hydrocarbons in question were conducted in 250ℓ 50.8 μm (2 mil) FEP Teflon bags. These bags were filled with hydrocarbon-free (<0.1 ppmC hydrocarbon) and NO_x-free (<1 ppb) air. The calculated amounts of terpenes and nitric oxide (NO) necessary to produce a given concentration (ppm) of each were injected into the air stream with a syringe while the bag was being filled. The rectangular chamber in which the Teflon bag was suspended between light banks was thermostated to 25° ± 1°C during the irradiations. For these experiments, 22 blacklamps (energy maximum 3660 A) and 4 sunlamps (energy maximum 3160A) were used. The light intensity, as measured by the photolysis of nitrogen dioxide (NO_2) in nitrogen (4), was 0.46 min^{-1}. The natural hydrocarbons were monitored by gas chromatography (GC) with the use of flame ionization detection. The NO_x and O_3 were measured by chemiluminescence instruments. Peroxyacetylnitrate (PAN) was monitored by gas chromatography with the use of an electron-capture detector. The oxygenated hydrocarbon products, such as acetaldehyde (CH_3CHO) and acetone ($(CH_3)_2CO$) were monitored by gas chromatography with the use of flame ionization detection. Wet chemical analysis spot checks were made for NO_2 and formaldehyde (H_2CO) with the use of the Saltzman (5) and chromatropic acid (6) methods, respectively. The purity of the terpenes was determined by gas chromatography, and when needed the terpenes were vacuum distilled to obtain the purest fraction. All other compounds were research grade and were used without further prepurification.

LONG PATH INFRARED STUDIES

For the long-path infrared studies, the photochemical chamber also served as an infrared absorption cell for *in situ* measurements. The chamber length was 9.1 m and the diameter was 0.31 m. The chamber was constructed of six borosilicate pipe sections, with sample inlets between each section. Plexiglas end plates and Teflon gaskets were used throughout. The volume of the chamber was 690ℓ, and it could be evacuated to less than one torr and operated at 760 torr. Surrounding each of the six sections were cylindrical light banks containing a total of 96 lamps. In these experiments, 48 blacklamps and 24 sun lamps were spaced evenly around the length of the chamber. The light intensity, as measured by the photolysis of NO_2 in nitrogen, was 0.51 min^{-1}. Samples were mixed and introduced into the chamber via a glass manifold.

The chamber contained an eight-mirror optical system to achieve long path lengths. An optical path of 357 m was used. A rapid-scan Fourier Transform Spectrometer that uses a Michelson interferometer, germanism-coated potassium bromide (KBr) beam splitter, and liquid-nitrogen-cooled detectors covered the spectral region of 700-3200 cm^{-1}. A more detailed discussion of the system and techniques used is given elsewhere (7).

RESULTS

SMOG CHAMBER EXPERIMENTS

The photooxidation of the natural hydrocarbons in Teflon bags was conducted at HC/NO_x ratios of approximately 3 and approximately 20 (ppm compound/ppm NO_x). The concentration of NO was kept constant at 0.33 ppm, and the hydrocarbon concentration was varied. Results for the HC/NO_x ratio of approximately 3 are listed in Table 1, in decreasing order of ozone formation. Also shown is the percent of hydrocarbon reacted at 60 minutes, and the time to reach one-half of the initial hydrocarbon concentration. In all cases, the oxidant maximum was reached before the end of the irradiation (200 min). The photooxidation of propylene, a commonly run compound used for smog-chamber validation, is included. The amounts of O_3 produced from cyclic terpenes ranged from 240 to 308 ppb, while the open-chain terpene myrcene produced 322 ppb; 556 and 642 ppb were produced from propylene and isoprene.

TABLE 1. HYDROCARBON REACTIVITY AND OZONE FORMATION

Compound	Ratio HC/NO_x	% HC reacted in 60 min.	Time (min) to reach $\frac{(HC)_i}{2}$	Max O_3 (ppb)
Isoprene	3.2	72	46	642
Propylene	3.0	50	60	556
P-cymene	3.2	27	128	450
Myrcene	3.2	89	21	322
D-limonene	2.7	96	40	308
Δ-carene	5.3	71	33	274
α-pinene	4.0	78	41	271
β-pinene	3.1	12	114	255
Terpinolene	2.8	98	34	240

Irradiations carried out at a HC/NO_x ratio of approximately 20 are shown in Table 2. The cyclic and open-chain terpenes at this ratio are again lower in O_3 production when compared to p-cymene and isoprene.

TABLE 2. HYDROCARBON REACTIVITY AND OZONE FORMATION

Compound	Ratio HC/NO_x	% HC Reacted in 60 min.	Max O_3 (ppb)
P-cymene	20.8	7	495
Isoprene	19.8	34	257
β-pinene	20.3	21	125
α-pinene	19.5	25	43
D-limonene	20.6	33	30
Terpinolene	21.3	34	15
Myrcene	20.3	27	1.5

The results of varying the HC/NO_x ratio while keeping (NO) = 0.33 ppm for the compound d-limonene are shown in Table 3.

LONG PATH INFRARED EXPERIMENTS

Irradiations in the long-path infrared cell were conducted at a HC/NO_2 ratio of 6.2-6.7 to determine the gas phase products resulting in the photooxidation. There is a depletion of the reactants during the photooxidation. A good material balance was not obtained. This fact is due to the inability of the infrared instruments to monitor aerosols suspended in the gas phase.

When isoprene (8 ppm) and NO_2 (1.3 ppm) were irradiated in the chamber, at 60 minutes, 68 percent of the isoprene had reacted. The major products observed were H_2CO, CH_3CHO, carbon monoxide (CO), carbon dioxide (CO_2), PAN, and formic acid (HCODH). Table 4 lists the percent of hydrocarbon reacted and products observed at 60 minutes. In the irradiation of isoprene, no strong bands or moderately absorbing bands were unidentified.

TABLE 3. EFFECT OF VARYING LIMONENE/NO_x RATIO ON MAX O_3 FORMATION

HC/NO_x Ratio	% HC reacted in 60 min.	Time (min) to reach $\frac{(HC)_i}{2}$	Max 0 (ppb)
0.14	71	38	295
0.45	63	48	251
0.63	50	60	364
1.13	83	48	430
2.25	95	43	410
2.70	96	40	320
4.53	88	35	219
4.93	90	31	204
20.6	33	NA	30

TABLE 4. REACTIVITY AND PRODUCTS BY LONG PATH INFRARED AT 60 MIN.

Compound	HC/NO_x ratio	% HC reacted	H_2CO	HCOOH	CO	CO_2	CH CHO	PAN	$(CH_3)_2CO$
β-pinene	5.3	58	0.94	0.39	0.23	0.4	0.05	0.018	0
Δ-carene	6.7	60	0.46	0.39	0.50	0.9	0.33	0.26	0
Isoprene	6.2	68	2.39	0.44	0.77	0.2	2.0	0.32	0
α-pinene	6.7	72	0.33	0.32	0.39	0.6	1.57	0.20	0
Myrcene	6.2	73	0.84	0.16	0.26	0.24	2.35	0.70	0.76
D-limonene	6.7	91	0.9	0.35	0.46	0.49	0.23	0.24	0
Terpinolene	6.2	95	1.2	0.31	0.49	0.69	0.35	0.28	0

Initial hydrocarbon conc. = 8 ppm
Products as ppm compound

Each of the other irradiated compounds had unidentified absorption bands. Unidentified absorption bands for the β-pinene photooxidation were a strong absorber at 1285 cm^{-1} and two moderately weak bands at 1650 and 1740 cm^{-1}. Other unidentified bands were: α-pinene, with moderate absorbing bands at 1230, 1280, 1375, 1650, and 2890 cm^{-1}; Δ-carene, with moderate bands at 855, 1375, and 1650 cm^{-1}; myrcene, with a strong band at 1842 cm^{-1} (acetone was identified as a product in this reaction); d-limonene, with weak bands at 855, 1630, and 1650 cm^{-1}; and terpinolene, with weak bands at 855, 1290, 1375, and 1630 cm^{-1}. The contribution to the material balance of these systems, if the chemical composition of the unidentified absorption bands were known, is minimal.

DISCUSSION

The carbon and nitrogen balance in all of the irradiations was poor. In the irradiation of d-limonene with the use of GC and wet-chemical methods, 3-20 percent of the initial carbon could be accounted for as observed products after the O_3 maximum had been reached. Infrared studies could account for only 4 percent of the carbon. The nitrogen balance in the Teflon bags accounted for 36-50 percent of the initial nitrogen while infrared studies could account for only 20 percent of the nitrogen. Results were similar for the other terpenes. The formation of aerosols when terpenes and NO_x are irradiated with UV light is well known (8). However, the mechanisms of formation and chemical composition of the aerosols are largely unknown. It is apparent that much of the carbon and nitrogen not accounted for is present in the aerosols.

A comparison of the data in Table 1 and 2 shows cyclic and open-chain terpenes lower in O_3 formation than p-cymene and isoprene. If a comparision is made of ozonolysis rates (9) to the decreasing order of O_3 maximum in Table 2, the compounds are arranged in increasing reaction rates from top to bottom. The only exception is terpinolene, whose ozonolysis rate is faster than myrcene. The apparent low O_3 formation of the terpene at higher HC/NO_x ratios seems to be due to the rapid reaction of newly formed O_3 by reaction with the terpenes.

Table 3 shows the results of maximum O_3 formation when the HC/NO_x ratio is varied for d-limonene. A dramatic maximum when plotted in formation is seen at a ratio of about 1.7. At this ratio or greater, the O_3 and d-limonene reaction is faster than O_3 formation processes.

CONCLUSION

When terpenes and NO_x are irradiated with UV, aerosols are formed that contain most of the initial carbon and nitrogen of the system. Little is known about the formation mechanisms and chemical composition of the aerosols. Gaseous products observed are aldehydes, CO, CO_2, HCOOH, $(CH_3)_aCO$, some compounds whose infrared spectra are unidentified, and, in all the terpenes studied, peroxyacetylnitrate. There is an optimum HC/NO_x ratio that results in a maximum formation of O_3. This optimum ratio is much lower than observed in the ambient rural air. Terpenes do react rapidly with O_3.

On the basis of present-day knowledge and field studies, which show very low concentrations of naturally emitted hydrocarbons, it is unlikely that naturally emitted hydrocarbons could be responsible for any significant fraction of oxidant formed in the urban areas. In rural areas, these hydrocarbons participate in aerosol or haze formation, while the significance of oxidant formation is probably also small. More experimental field and laboratory work is necessary before final conclusions can be reached, due to the extremely high HC/NO_x ratio observed in rural areas. This ratio is far too large to produce any significant O_3 levels. All of the O_3 produced would necessarily have to react with the excess terpenes available.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to Mr. Theodore Winfield for his assistance in the smog chamber experiments.

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MEASUREMENT OF PHOTONS INVOLVED IN PHOTOCHEMICAL OXIDANT FORMATION

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ABSTRACT

We have considered a photolysis of the molecules nitrogen dioxide, ozone, nitrous acid, formaldehyde, hydrogen peroxide, and nitric acid, which are important to air pollution modelling. Estimates of their photolysis rates were made from known parameters. Experimental techniques to determine these rates have been devised and tested for nitrogen dioxide, nitrous oxide, and ozone. Extensive results for nitrogen dioxide and some preliminary data on ozone are presented.

INTRODUCTION

Photochemical smog is intrinsically dependent on the solar flux. The rate of photolysis (J) of any pollutant present in small concentrations is given by the formula:

$$J = \int_0^\infty I(\lambda)\, \Phi(\lambda,T)\, \varepsilon(\lambda,T) d\lambda \qquad (1)$$

where $I(\lambda)$ is the time and wavelength-dependent solar flux, $\Phi(\lambda,T)$ is the temperature and wavelength-dependent dissociation quantum yield, and $\varepsilon(\lambda,T)$ is the photon absorption cross-section. While in principal all the above parameters can be measured a priori and the result can be calculated for any given model, there are for some molecules significant uncertainties in the appropriate structured integral over λ. Thus, it is best to measure any important rates directly to compare with theory.

MOLECULES CONSIDERED

Several molecules that have been identified as being of importance in photochemical smog are listed in Table 1. The theoretical rate of photolysis averaged over 24 hours and one year at 30°N is given for each molecule.

We have determined an experimental technique whereby each of these rates may be determined in situ using flow actinometers. The methods are summarized in Table 2.

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TABLE 1. THEORETICAL RATES OF PHOTOLYSIS (AVERAGED OVER 24 HOURS AND ONE YEAR AT 30° N) FOR IMPORTANT PHOTOCHEMICAL SMOG MOLECULES

Reaction	Javg sec^{-1}	Ref.
$NO_2 + h\nu \rightarrow NO + O$	3.1×10^{-3}	Hampson
$O_3 + h\nu \rightarrow O^1D + O_2$	5.1×10^{-6}	De More
$CH_2O + h\nu \rightarrow H + CHO$	9.4×10^{-6}	Calvert
$HONO + h\nu \rightarrow OH + NO$	3.1×10^{-4}	Levy
$H_2O_2 + h\nu \rightarrow 2OH$	9.0×10^{-7}	Schumb
$HNO_3 + h\nu \rightarrow OH + NO_2$	5.5×10^{-7}	Levy

TABLE 2. EXPERIMENTAL TECHNIQUES FOR MEASURING THE RATES OF PHOTOLYSIS OF SELECTED MOLECULES IN SITU WITH FLOWING ACTINOMETERS

Molecule	Flowing Gas	Method
NO_2	Air/NO_2	Measure NO by chemiluminescence.
O_3	N_2O/O	Measure NO by chemiluminescence.
CH_2O	N_2/CH_2O	Measure H by resonance fluorescence.
HONO	HCl/HONO	Measure NO by chemiluminescence.
H_2O_2	HCL/H_2O_2	Measure Cl by resonance fluorescence.
HNO_3	Air/HNO_3	Measure NO by chemiluminescence with converter.

DETAILS OF THE NITROGEN DIOXIDE STUDIES

Nitrogen dioxide (NO_2) is the most important photochemically active molecule in photochemical smog (1, 2, 3). Therefore, we have worked on measurement of J(NO_2) for some time. In the earlier studies, Jackson et al. (4) prepared the first flow actinometer. In brief, Jackson measured J_1 by exposing a 1 ppm NO_2 flow for four seconds to direct sunlight through an ultraviolet (UV) transparent quartz tube. The resulting production of [NO] in the air stream gave an indication of J_1 through the kinetics of the following reaction:

$$d[NO]/dt = J_1[NO_2] \tag{2}$$

$$J_1 = \frac{\Delta NO}{[NO_2]_o} \frac{1}{\Delta t} \tag{3}$$

where ΔNO is the increase in the nitric oxide (NO) concentration of the air stream after exposure to the sun, $[NO_2]_o$ is the initial NO_2 concentration, and Δt is the exposure time.

Jackson plotted his measured J_1 against an Eppley UV pyranometer output (4) that had a spectral sensitivity range that overlapped the NO_2 spectrum. A straight line correlation was obtained with considerable scatter where $J_1 = 0.019 \pm 0.02$ E, E being the Eppley reading in watts meter^{-2}. Further engineering improvements made recently on the apparatus produced data that shows a curved correlation between measured J_1 and the Eppley output. Problems not considered by Jackson, concerning the Eppley and NO_2 absorption overlap, background surface albedoes, the Eppley's cosine response and inherent errors in relation 9, can account for the curvature seen in the new data.

AN IMPROVED ACTINOMETER

A schematic of the new actinometer is shown in Figure 1. Two 60 Hz diaphragm pumps, arranged in parallel to enhance the flow, pushed ambient room air into the system. The stream of air is first passed through a drying agent and into a constant temperature enclosure containing the NO_2 source, a permeation tube containing liquid NO_2. This permeation device was usually operated at 34°C. It was necessary to dry the air passing over the permeation tube in order to keep the background NO level in our airflow low. The following reactions were probably giving rise to the unsteady and unacceptably high NO/NO_2 ratio of 0.005 that was originally observed:

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

$$2HNO_2 \rightarrow NO + NO_2 + H_2O$$

Based on tabulated thermodynamic data and assuming that pure NO_2 permeates, we find that

$$[NO]/[NO_2] = k[H_2O]^{1/3}$$

where $k \sim 0.1$ atm$^{-1/3}$. Thus, at normal $[H_2O]$ of 0.01 - 0.02 atm, $[NO]/[NO_2] \sim 10^{-5}$ atm., then with the one-third power dependence one would expect a tenfold reduction in $[NO]/[NO_2]$. The observed values indicate qualitative agreement with this mechanism and show that water (H_2O) must be avoided if pure NO_2 in air is required.

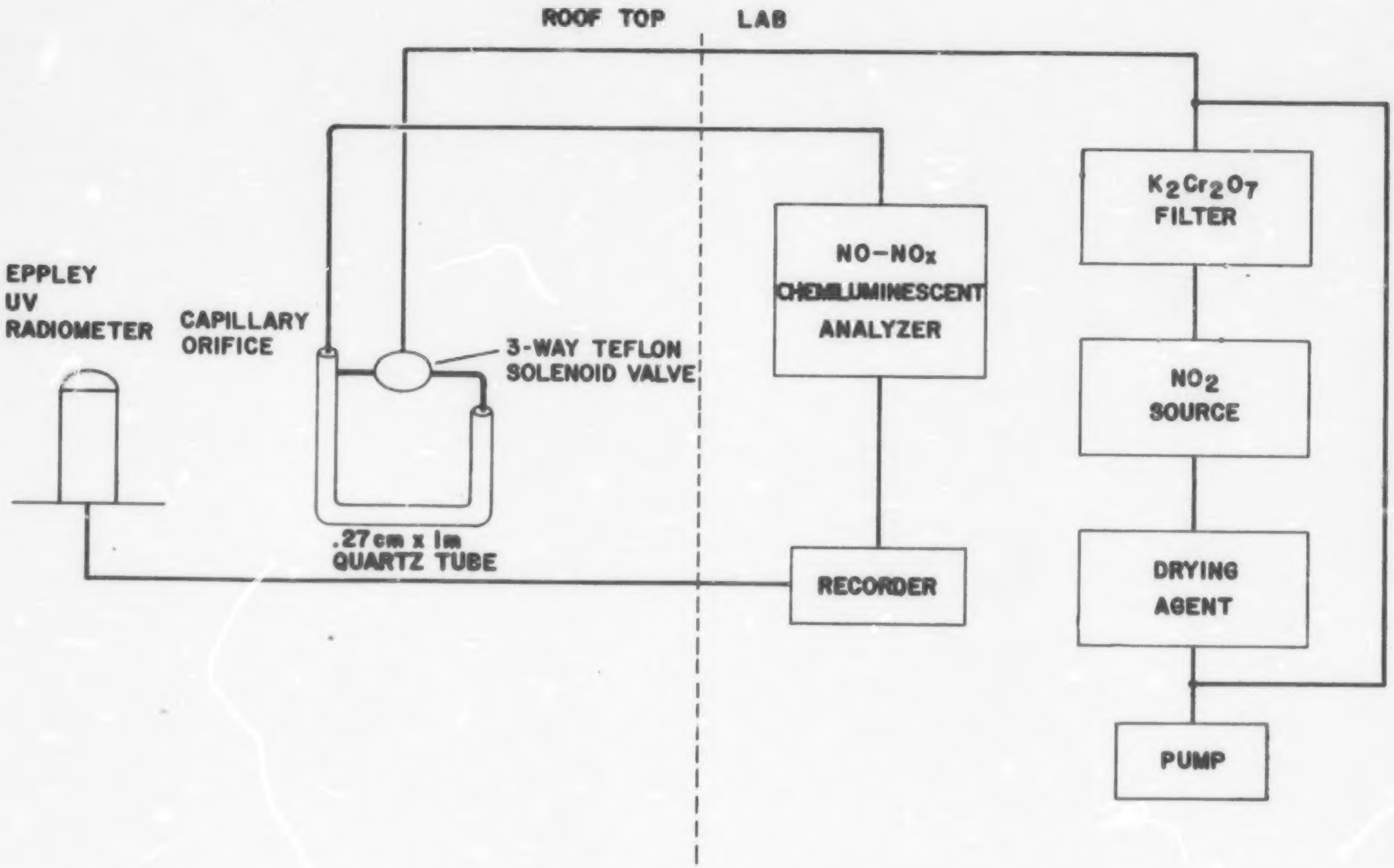

Figure 1. A schematic diagram of the improved actinometer and the Eppley with which it is compared.

Using dried air and a potassium dichromate ($K_2Cr_2O_7$) impregnated filter for NO → NO_2 conversion (6), we were able to bring our NO/NO_2 ratio down to a steady, acceptable 0.001. A by-pass around the drying agent – constant temperature box -$K_2Cr_2O_7$ filter can be included, as shown, in order to prolong the life of the drying agent and $K_2Cr_2O_7$ filter.

The airflow was then passed in teflon through a flow meter and outside the building to the photolysis chamber, which was a 0.27 cm radius, 1-meter long quartz tube bent in a u-shape. A three-way teflon solenoid valve was placed between the two ends of the quartz tube. One position of the valve bypassed the quartz tube and directed the stream of air directly to our nitrogen oxides (NO_x) detector, a Thermo-Electron model 12A chemiluminescent analyzer altered for direct capillary inlet to the vacuum system. The other setting of the valve sent the flow through the quartz tube to the NO_x detector. Thus, the same capillary was used to monitor both the background $[NO_2]$ and ΔNO. The quartz tube was suspended approximately one foot above a 4'x6' horizontal white plywood board to achieve a constant albedo background.

The entire plumbing was made from teflon or glass. Metal was avoided because of the corrosive properties of NO_2. Care was also taken to make sure that our air stream was in complete darkness except when passing through the quartz tube. The exposure time, Δt, to the sun can be controlled by either adjusting the pump speed or adjusting the length of the quartz tube exposed to the sun. Adjusting the NO_2 concentration in the air stream can be accomplished by either changing the pump speed or the permeation tube temperature. Thus, there are more than enough variables to obtain any NO_2 concentration and exposure time Δt desired. Typically we used a Δt of 0.734 sec., and an NO_2 concentration around 24.6 ppm; this gave the most error-free approximation of J_1 from Equation 3. Calibrations were taken on $[NO_2]_o$, background NO, and flow speed every 90 minutes.

Keeping a steady flow speed and obtaining a steady, low background NO level were the most difficult variables to control, the probable error in the total system being ± 6 percent.

MINIMIZATION OF THE ERRORS IN EQUATION 3

If all other factors entering into the flow actinometer photolysis are taken into account, then a system can be built in which systematic errors almost totally cancel. The resultant $[NO_2]_o$ used is 25 ppm with a flow time of 0.75 sec. Note that since

$$\frac{\Delta NO}{[NO_2]}$$

is used to define J_1 from Equation 3, the absolute calibration of the NO_x meter is not an important parameter to the first order. Instead, the 100% conversion in the NO_x converter is more important, and can be tested as described by Stedman (7).

ACTINOMETER VERSUS EPPLEY RESPONSE

We have established a definite curved correlation between the actinometer measurement of J_1 and the UV Eppley photometer measurements as seen in Figure 2. The points represent data taken between noon and sunset on a clear day at Ann Arbor, Michigan, June 4, 1976. The line in Figure 2 represents a theoretical prediction which agrees well with the data points, considering that the line is completely independent of the points and depends only on the calibration factors supplied by Eppley and traceable to NBS.

The theoretical determination of J_1 as a function of zenith angle θ was made using the formulation of Leighton as described by Stedman et al. (3). Similarly, the Eppley photometer reading, E, in mwatts cm^{-2}, was determined from

$$E = \int_{\lambda\,min}^{\lambda\,max} (\cos(\theta)\ Id(\lambda,\theta) + 1/2 I_s(\lambda,\theta))d\ ,$$

where $\lambda_{max} = 385$ nm and $\lambda_{min} = 290$ nm define the limits of the Eppley action spectrum, I_d and I_s are the direct and scattered radiation reaching the ground, respectively, and $(\cos\theta)$ and (1/2) take into account the cosine response of the Eppley photometer. (Note that we have assumed the scattered radiation to be homogeneous over the hemisphere.) I_d and I_s were calculated using the formulation of Leighton (1).

The dominant factor determining the shapes of our theoretical line in Figure 2 is the Eppley photometer's cosine response for the hemisphere directly overhead, whereas the actinometer is equally sensitive to light from all directions. This correlation will hold for any location provided that the weather is clear. The effect of cloudiness is shown in Figure 3. One set of points represents data taken with clear skies from sunrise to about 8:30 a.m. EDT. Clouds began moving in after 8:30, with overcast conditions prevailing after 11:30 a.m. A definite curved relationship can be seen between the Eppley observed light coming directly from the sun. Later, overcast conditions diffuses the sunlight more evenly over the hemisphere of the sky, and the resulting decrease in total sunlight reaching the ground can be seen in a resulting linear decrease in measured J_1 between 11:30 a.m. and 1:30 p.m., usually a time of roughly constant J_1.

The mismatch of the Eppley and actinometer spectra could result in a slight curvature of the Eppley-actinometer relation. The Eppley responds to a wavelength peak at 360 nm whereas the NO_2 action spectrum peaks at 400 nm. The result is that the Eppley is again more sensitive to the solar zenith than the actinometer (1).

J_1 FROM EPPLEY MEASUREMENTS

Based upon data presented earlier in this report, Figure 2 will give accurate J_1 values from a known UV photometer output for a given solar zenith

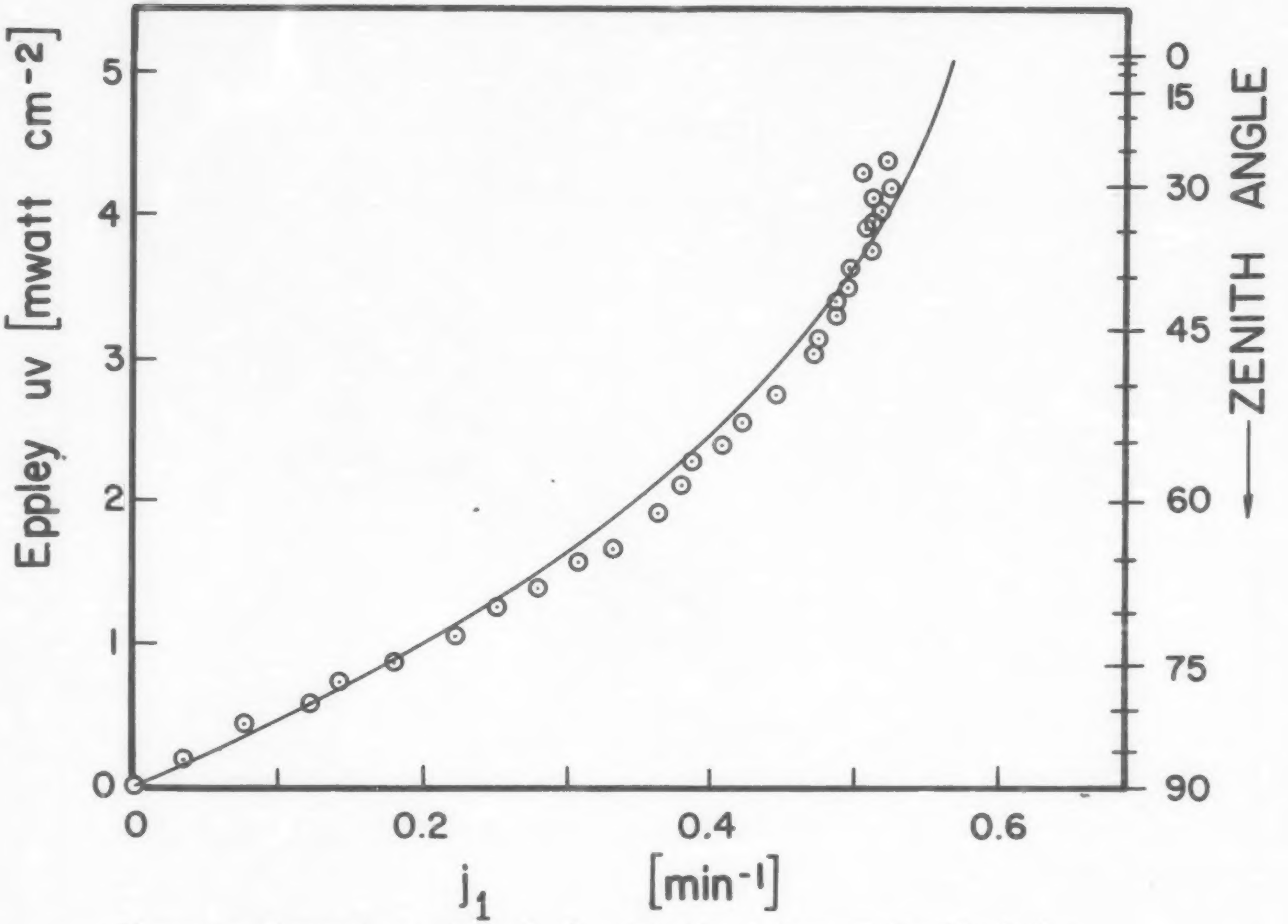

Figure 2. Observed and theoretical correlation between Eppley UV reading and directly measured J_1 for a clear sky. Data was taken between 12 noon and sunset in Ann Arbor, June 4, 1976. Eppley readings are given with the maximum zenith angle possible for that reading.

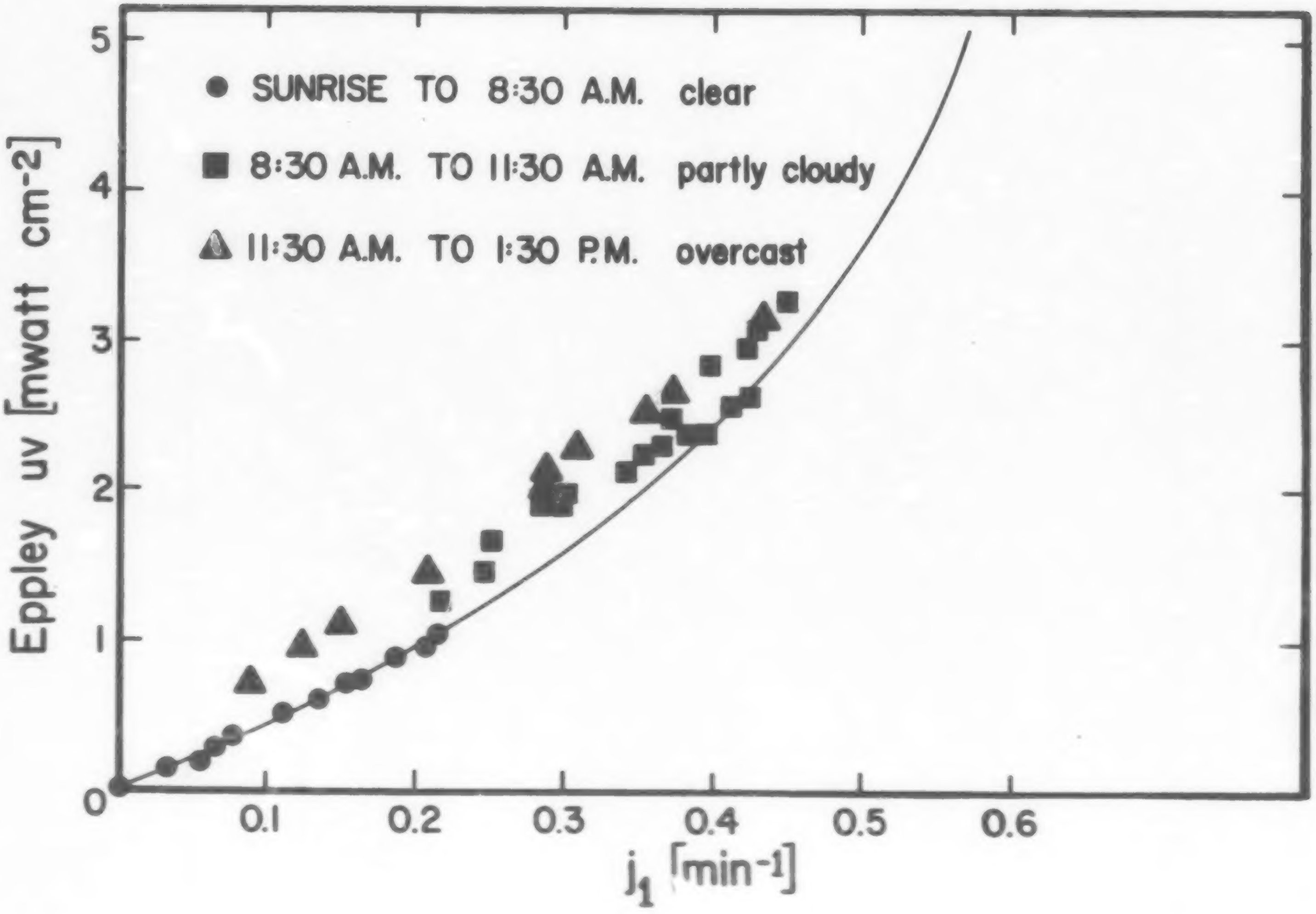

Figure 3. Observed correlation between Eppley and actinometer on May 28, 1976. The line is the theoretical prediction for a clear day from Figure 2.

angle on a clear day. On a cloudy day we can make an approximation that overcast conditions behave like an opaque isotropic wedge filter, i.e., they give a linear relation between J_1 and Eppley as illustrated by the triangles in Figure 3. Clearly, this will not be absolutely correct, but the data of Figure 3 show that it is a reasonable approach to the difficult problem of variable cloudiness. Thus to find J_1, find the value of Eppley reading (E_{max}) and associated J_1 (J_{max}) which would hold for a clear day (either from previous data in the same location or from the known solar zenith angle shown in Figure 2). Then J_1 = (Eppley reading) x J_{max}/E_{max}. If working in an area of high surface albedo (a), all data-derived J_1 should be multiplied by (1 + a), where a is obtainable by direct measurement or by estimation from the data in Table 1.

We recently received a report from L. Zafonte, P. O. Rieyer, and J. R. Holmes of the California Air Resources Board (8). They have been using a similar apparatus, and report similar values of J_1. They do not optimize the intrinsic chemical errors in their system by our technique, but rather correct for their errors by using the known reaction rates.

MEASUREMENTS OF OZONE PHOTOLYSIS

There are two processes in the photolysis of ozone (O_3). The most important is the production of $O(^1D)$ in the near ultraviolet, since $O(^1D)$ is an important source of atmospheric hydroxyl (OH) radicals:

$$O_3 + h\nu\ (300 - 310\ \text{nm}) \rightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \rightarrow 2OH$$

The actinometer that we have devised depends on the reaction of $O(^1D)$ with nitrous oxide (N_2O). We photolyse a stream of N_2O with a small amount of O_2/O_3 mixture. The reaction scheme is

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2$$

$$\rightarrow 2NO$$

With equal rates on both paths, the yield of NO formation per $O(^1D)$ is taken to be unity. The NO continues to oxidize thus:

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O_2 \rightarrow NO_3 + O_2$$

$$NO_2 + NO_3 \rightleftarrows N_2O_5$$

$$N_2O_5 + H_2O \rightleftarrows 2NHO_3$$

The problem is then to measure the NO_x yield in the presence of excess

O_3. We have tried a number of routes and a reasonably successful method is to decompose the O_3 and higher oxides at 350-400°C on a platinum/aluminum oxide (Pt/Al_2O_3) catalyst, followed by conversion to NO in a ferrous sulfate ($FeSO_4$)-packed trap. Measured data are still preliminary but are in the same range as our theoretical predictions based on our most recent $\Phi(\lambda,T)$.

ACKNOWLEDGEMENT

We acknowledge the support of NSF under grant #ATM76-03793.

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ACTINIC SOLAR FLUX AND PHOTOLYTIC RATE CONSTANTS IN THE TROPOSPHERE

J. T. Peterson, K. L. Demerjian, K. L. Schere*

ABSTRACT

The results of detailed theoretical calculations of the volumetric flux of solar radiation in the atmosphere are discussed, and the development of a generalized scheme to apply those data to the calculation of photolytic rate constants over a diurnal period is described. The vertical variation of the rate constants for nitrogen dioxide and formaldehyde through the lowest several kilometers of the atmosphere is emphasized. Because of changes in solar flux, these rate constants are typically 20 to 70 percent greater at 1 km altitude than at the earth's surface, for example. The theoretically derived rate constants were compared to similar ambient measurements and there was good agreement between them. The results presented here have relevance to photochemical air quality simulation models and smog chamber studies.

INTRODUCTION

Important parameters of photochemical air quality simulation models and smog chamber studies are the rate constants (k) for the photodissociation of certain species. They describe the rate (time $^{-1}$) at which a molecule dissociates when irradiated by ultraviolet (UV) solar radiation. Since k is directly dependent on incident solar intensity, it provides a link between solar radiation and air quality levels in both mathematical models and chamber studies. Thus, accurate knowledge of the spatial, diurnal, and annual variability of k throughout a metropolitan atmosphere is necessary in various studies of photochemical air pollution. This paper describes the results of recent detailed calculations of solar radiant energy in an urban atmosphere and the development of a generalized scheme to use the radiation values to calculate photolytic rate constants over a diurnal period. The rate constants for nitrogen dioxide (NO_2) and formaldehyde (H_2CO) are emphasized.

RADIATIVE FLUX COMPUTATIONS

For photochemical applications, the direction at which solar radiation is incident upon an NO_2 molecule is of no concern. The primary consideration is the flux through a spherical volume, rather than that through a plane horizontal surface, which is used for most geophysical applications. Thus, this actinic, or volumetric, flux is the sum of the radiative intensity over all angles of incidence and represents the solar radiation that would be incident on an ensemble of molecules with random orientations.

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The actinic solar flux for a model atmosphere has been calculated for solar zenith angles for 0° to 86° and for wavelengths from 290 to 700 nm (Peterson, 1976a). A detailed radiative transfer model, based on the work of Braslau and Dave (1973), was used for the flux computations at 40 model levels from the earth's surface near sea level to the top of the atmosphere. Aerosol scattering and absorption, ozone absorption and Rayleigh scattering were accounted for. Total atmospheric ozone was assumed to be 0.295 cm-atm. The normal optical thickness of the aerosols was 0.254 to 500 nm wavelengths. This corresponds to annual average nonurban conditions over the eastern U. S. and is slightly less than that for annual average U.S. urban conditions (Flowers et al., 1969). It also corresponds to conditions in Los Angeles on "clean" days during the smog season (July through October). Thus, the calculations were based on typical aerosol amounts so that computed actinic fluxes would have general applicability.

PHOTOLYTIC RATE CONSTANT COMPUTATIONS

A generalized scheme and computer program for calculating photolytic rate constants has been developed by Schere and Demerjian (1976). It uses as input the actinic flux values, J, described above, in addition to the absorption cross section, σ, and primary quantum yield, ϕ, for each species. For a particular species, i, the rate constant for photodissociation in the lower atmosphere, is expressed as follows:

$$k_i(\theta,h) = \sum_\lambda J(\lambda,\theta,h) \cdot \sigma_i(\lambda) \cdot \phi_i(\lambda) \ , \qquad (1)$$

where θ is solar zenith angle, h is the height above ground and λ is wavelength. Values of σ and ϕ have been compiled for seven species which dissociate when exposed to radiation from 290 to 800 nm wavelength: NO_2, nitrous acid, (HONO), nitric acid ($HONO_2$), O_3, H_2CO, hydrogen peroxide (H_2O_2), and acetaldehyde (CH_3CHO). Specific reactions considered were:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (2)$$

$$HONO + h\nu \rightarrow HO + NO \qquad (3)$$

$$HONO_2 + h\nu \rightarrow HO + NO_2 \qquad (4)$$

$$O_3 + h\nu \rightarrow O(^3P) + O_2 \qquad (5)$$

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (6)$$

$$O_3 + h\nu \rightarrow O_2(^1\Delta) + O \qquad (7)$$

$$H_2CO + h\nu \rightarrow H + HCO \qquad (8)$$

$$H_2CO + h\nu \rightarrow H_2 + CO \quad (9)$$

$$H_2O_2 + h\nu \rightarrow 2HO \quad (10)$$

$$CH_3CHO + h\nu \rightarrow CH_3 + HCO \quad (11)$$

$$CH_3CHO + h\nu \rightarrow CH_4 + CO \quad (12)$$

The user-oriented computer program for calculating photolytic rate constants was developed to provide output for a diurnal solar cycle. Rate constants are first generated for the specific zenith angles for which actinic flux values are available, i.e., 0, 10, 20, 30, 40, 50, 60, 70, 78, and 86°. Actual solar zenith angles are then calculated for the diurnal period for a specified location and date. Finally, the corresponding rate constants are determined throughout the diurnal period by using a cubic spline fit to interpolate for any zenith angle.

The rate constant program is formulated to calculate values for the lowest tens of meters near the earth's surface. However, actinic flux data are available for ten additional levels of the radiative transfer model: 0.15, 0.36, 0.64, 0.98, 1.38, 1.84, 2.35, 2.91, 3.53, and 4.21 km above the surface. The actinic flux values at each zenith angle for these levels can be supplied to interested readers upon request.

RESULTS

Since the wavelength-dependent absorption coefficients and quantum yields for any species are fixed, the variation of that species' rate constant in space and time depends solely on the variability of the actinic flux. Besides its diurnal dependence, the actinic flux is also sensitive to changes of surface albedo, atmospheric total O_3 amount, cloudiness, surface elevation, atmospheric aerosol concentrations, and altitude above the surface (Peterson 1976a). This last factor--the altitudinal dependence of actinic flux--is itself strongly dependent on aerosol concentrations and their change with height.

In the ultraviolet spectral region, the total actinic flux generally increases with height through the lowest five to ten kilometers of the atmosphere. The upward- and downward-directed actinic components show similar height dependence. The downward component typically exhibits its greatest rate of change near the surface, where it is depleted by absorption and back-scattering from high aerosol and pollutant concentrations. The upward component also increases rapidly with height near the earth's surface because of the low reflectivity of the earth (typically about 5% in the ultraviolet) and the large amount of aerosol and Rayleigh scattering. But, because of its small absolute value, the upward component has only a minor effect on the percentage change with height of the total actinic flux.

Of the several species listed previously which dissociate when exposed to sunlight, NO_2 and H_2CO are two of the most important for photochemical air pollution (Dodge and Hecht, 1975). Equation 1 was evaluated for these compounds for each 10 nm wavelength interval using the actinic flux at the earth's surface and 40° zenith angle. The results were normalized for each species to a maximum value of 1.0. The resulting wavelength sensitivity of the two rate constants is shown in Figure 1. The sensitivity of the rate constants at the shortest wavelengths goes to zero parallel with the amount of incident UV radiation. In each case, the long wavelength cutoff is determined by the respective quantum yield and absorption cross-section. The H_2CO rate constant is sensitive to a rather narrow spectral interval centered at about 330 nm. In contrast, the NO_2 rate constant responds to a much broader spectral and region longer wavelength. The importance of this difference in wavelength sensitivity will be discussed below.

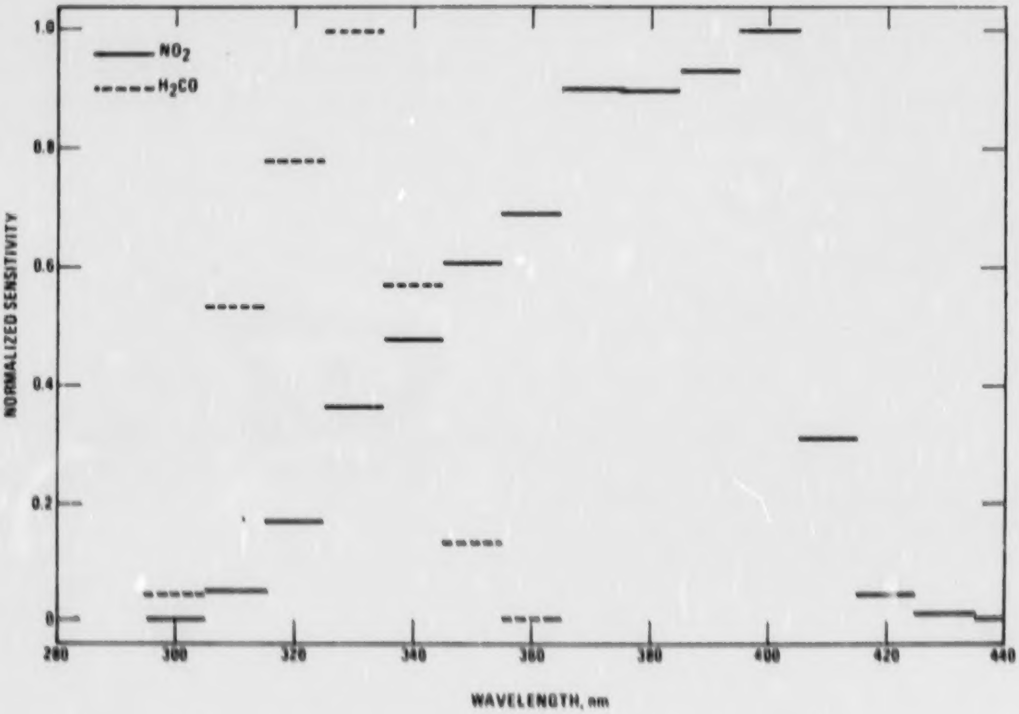

Figure 1. Normalized sensitivity of photodissociation rate constants for NO_2 (solid) and H_2CO (dashed) versus wavelength. For each species, the wavelength dependent values were obtained from the product of absorption cross section, quantum yield, and actinic flux at the earth's surface for 40° zenith angle.

Using Equation 1, the photodissociation rate constants for NO_2 (Equation 2) and H_2CO (Equation 8) were calculated as a function of zenith angle for the surface and first ten model levels above the surface. Selected results are presented in Tables 1 and 2 for NO_2 and H_2CO, respectively, and in Figure 2 for NO_2. Because of the change of actinic flux with height, the rate constants for both species show significant increases with height. The rate constants generally increase with height and zenith angle, except for the 86° case. For NO_2, for example, k is 21 to 70% greater at 0.98 km than at the surface, depending on zenith angle. Corresponding percentage increases for H_2CO are even greater for zenith angles of 79° and less, but are smaller for the largest zenith angle.

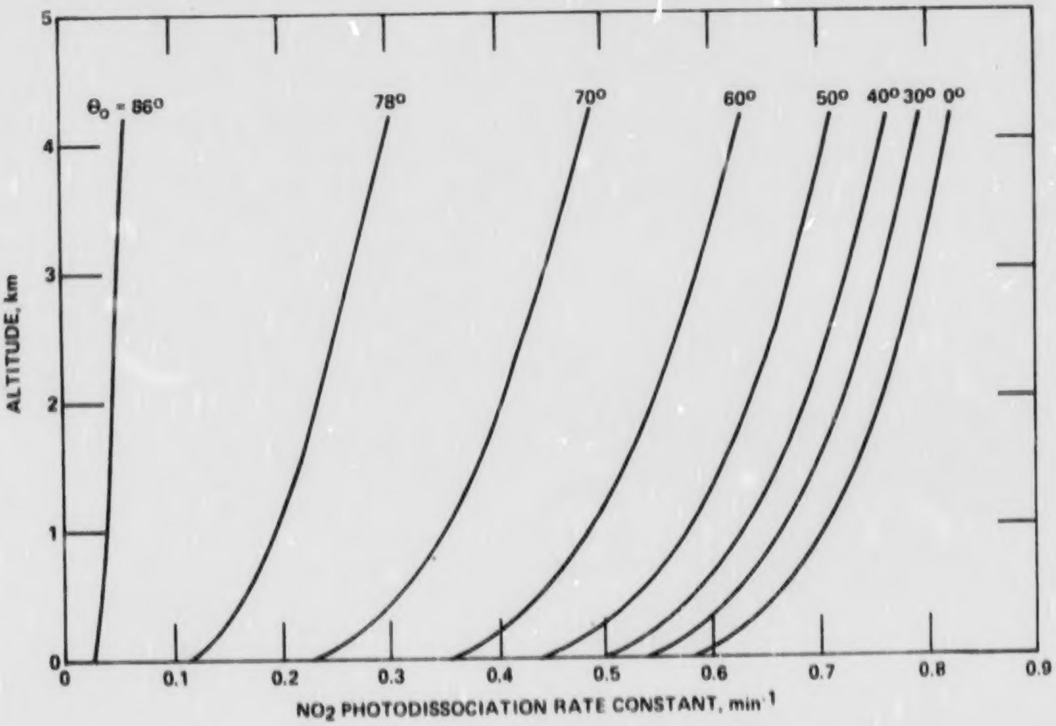

Figure 2. Calculated NO_2 photodissociation rate constants as a function of altitude and solar zenith angle (θ_o).

The differences between the NO_2 and H_2CO rate constant increases from the surface to higher atmospheric levels result primarily from the different wavelength sensitivity of the two species. As shown in Figure 1, H_2CO responds more to shorter wavelength radiation than does NO_2. Since Rayleigh (molecular) scattering depends on the inverse fourth power of wavelength, the shorter wavelength energy undergoes more depletion while passing through the atmosphere.

The increased values of the rate constants above the surface can be quite significant for ground level pollutant concentrations. For example, precursor pollutants emitted aloft, such as from a tall chimney, into a stable atmospheric layer will be exposed to more solar radiation than near the surface. If subsequent increases occur in the mixing height, reaction products of pollutants trapped in stable layers can be mixed downward to the surface. In another example, precursor pollutants emitted near the surface can be transported aloft and be exposed to more intense radiation when vertical mixing is occurring in the lower atmosphere. Subsequently, the reaction products can be transported back to the surface.

TABLE 1. CALCULATED VALUES OF NO_2 (Equation 2) PHOTODISSOCIATION RATE CONSTANT (min^{-1}) AT THE EARTH'S SURFACE (line 1): PERCENTAGE INCREASE OF THE RATE CONSTANT FROM THE SURFACE TO VARIOUS ATMOSPHERIC HEIGHTS (lines 2-7)

HEIGHT	ZENITH ANGLE (°)									
	0	10	20	30	40	50	60	70	78	86
SURFACE	0.579	0.574	0.560	0.535	0.496	0.438	0.352	0.231	0.114	0.025
0.15 km	6.0	6.1	6.4	6.9	7.7	8.9	11.1	14.3	16.7	8.0
0.36 km	11.4	11.5	12.1	13.1	14.5	16.9	21.0	27.7	34.2	20.0
0.64 km	16.6	16.9	17.7	19.1	21.2	24.4	30.4	40.7	52.6	36.0
0.98 km	21.4	22.0	22.9	24.7	27.2	31.5	39.2	52.8	70.2	48.0
1.84 km	29.9	30.3	31.6	34.0	37.7	43.4	53.7	73.2	101.	72.0
2.91 km	36.4	37.1	38.2	41.7	46.2	53.7	66.5	91.8	132.	100.

TABLE 2. CALCULATED VALUES OF H_2CO (EQUATION 8) PHOTODISSOCIATION RATE CONSTANT (MIN^{-1}) AT THE EARTH'S SURFACE (LINE 1) (ALL ENTRIES $X10^{-3}$); PERCENTAGE INCREASE OF THE RATE CONSTANT FROM THE SURFACE TO VARIOUS ATMOSPHERIC HEIGHTS (LINES 2-7)

HEIGHT	ZENITH ANGLE (θ°)									
	0	10	20	30	40	50	60	70	78	86
SURFACE	2.18	2.15	2.05	1.88	1.64	1.32	0.934	0.507	0.211	0.040
0.15 km	8.0	8.0	8.3	8.8	9.5	10.2	12.0	13.6	13.5	11.6
0.36 km	15.8	15.9	16.4	17.4	18.8	20.9	23.8	27.4	27.7	22.7
0.64 km	23.7	23.8	24.6	26.1	28.2	31.3	35.9	41.7	42.8	34.1
0.98 km	31.6	31.7	32.8	34.6	37.5	41.7	47.9	56.3	58.7	45.6
1.84 km	46.0	46.3	47.9	50.6	54.8	61.1	70.8	84.6	90.2	66.9
2.91 km	58.3	58.7	60.8	64.5	70.2	78.9	92.5	114.	126.	89.3

An alternate way of presenting the height dependence of the photodissociation rate constant is shown in Figure 3. The diurnal variation of k_{NO_2} was calculated for Los Angeles, California, on September 1, using the actinic flux for the surface and at 0.98 km (fourth model level). Although the largest absolute differences are during midday, the greatest percentage changes occur during early morning and late afternoon. Thus, these data show that photochemical reactions generally take place at a significantly faster rate 1 kilometer above the earth than at the surface.

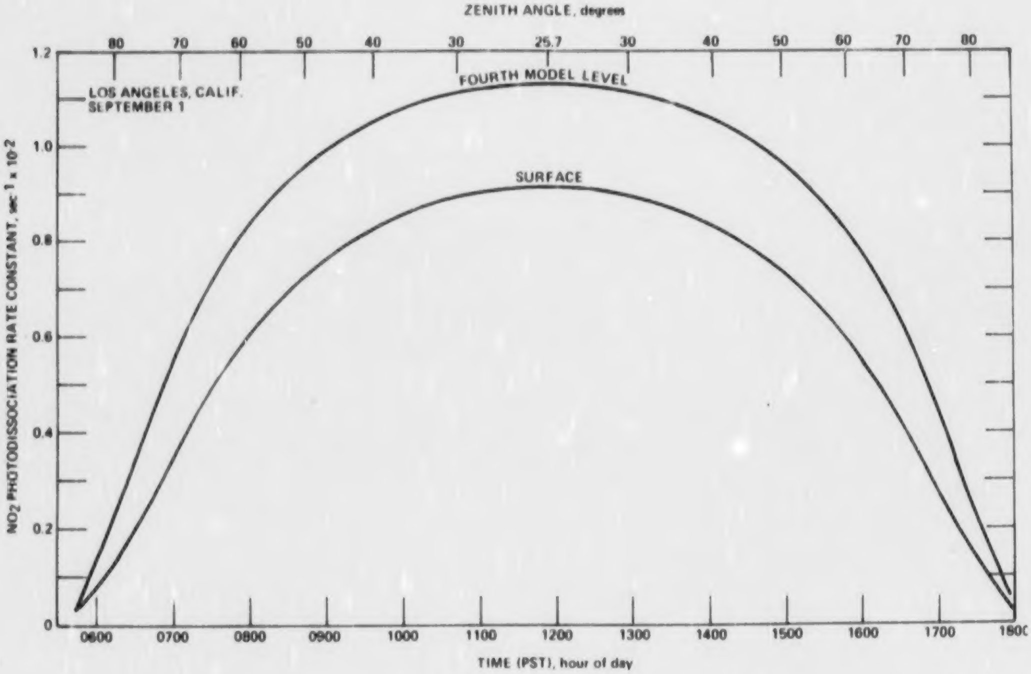

Figure 3. Calculated NO_2 photodissociation rate constants versus time for Los Angeles, California on September 1 for the earth's surface and 0.98 km above the surface (fourth model level).

The results presented in the previous discussion were derived from calculated actinic fluxes based on average atmospheric aerosol characteristics typical of eastern U.S. nonurban conditions. In reality, aerosol concentrations over metropolitan areas are often two or three times greater than our model values. Consequently, the vertical gradient of actinic flux, and hence the altitudinal change of rate constants, is often substantially greater than that shown above (Peterson, 1976b). In fact, for aerosol concentrations double those used here, the increase of k from the surface to 0.98 km was calculated to range from 29% for a zenith sun to 103% for a solar zenith angle of 78°.

The rate constant data previously described have all been theoretically generated. To test the overall reliability of our computational scheme, independent measures of the NO_2 rate constant were obtained by Research Triangle Institute personnel exposing a chemical actinometer to sunlight using the technique of Sickels and Jeffries (1975). An example of the comparison between the rate constants measured with the actinometer and calculated by the method described herein is shown in Figure 4. A more complete comparison is discussed by Schere and Demerjian (1976). The circles represent the measured values. The dashed line represents rate constants calculated for cloudless conditions. Since clouds were present on this day (April 23, 1975), the calculated values were adjusted downward by the ratio of the measured UV radiation on this day to the measured UV radiation during an adjacent cloudless day. Although the data have considerable scatter, the two sets of data evince general agreement.

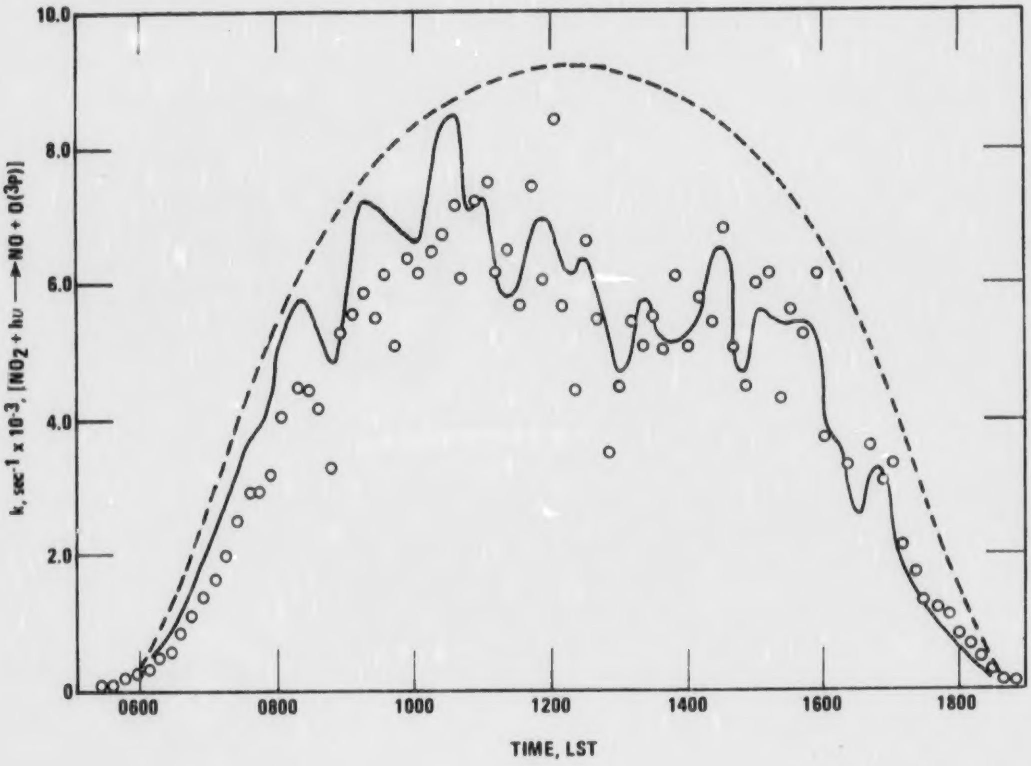

Figure 4. NO_2 photodissociation rate constants versus time for Research Triangle Park, North Carolina on April 23, 1975. Circles represent five-minute average values measured with a chemical actinometer. Dashed line represents calculated values for cloudless conditions. Solid line represents calculated values for prevailing cloudiness conditions.

Another set of empirical NO_2 rate constant data has been recently published by Zafonte (1976) for El Monte, California, 17 miles east of Los Angeles. During June and July 1975, he obtained a maximum value of about 0.55, based on a measurement of UV radiation. During midsummer the noontime solar zenith angle at Los Angeles is about 10°. The corresponding calculated rate constant for the surface is 0.574 (see Table 1). However, even though the uncertainty in the calculated values exceeds several percent when they are applied to a specific situation, a small correction (-3.2%) should be applied to the calculated rate constants to account for the greater than average earth-sun distance during that time of year. The resulting measured-calculated rate constant agreement is remarkably good.

DISCUSSION

Two recent studies using the photochemical diffusion model developed by Systems Applications, Inc. (SAI) have shown that computed O_3 concentrations in the Los Angeles Basin are quite sensitive to incident solar radiation as it affects k_{NO_2} (Peterson and Demerjian, 1976; Liu et al., 1976). However, in the SAI model, k_{NO_2} is invariant with height. In view of the large variation of k_{NO_2} with height discussed above, we recommend that photochemical models be tested for their sensitivity to vertical changes of radiation-dependent rate constants. In the two reports mentioned, solar radiation was linked to computed pollutant concentrations only through k_{NO_2}. Photochemical models with improved kinetic mechanisms including other species subject to photodissociation, such as H_2CO, are are now being developed. Since species like H_2CO, which respond to short wavelength UV radiation, are more dependent on altitude than k_{NO_2}, the improved models may show even more sensitivity to the spatial variations of solar radiation.

The results presented in this paper also have relevance to smog chamber studies. Zafonte (1976) has suggested that typical k_{NO_2} values in chambers and the length of time for chamber runs usually do not agree with k_{NO_2} values measured near the earth's surface. Our calculations indicate that the discrepancy between ambient and chamber k_{NO_2} levels is even greater for the top of the mixed layer compared to that at the earth's surface. Our data also point out the necessity to maintain continual measurements and calibrations of radiation levels as a function of wavelength within chambers. Photodissociation rates for NO_2 and H_2CO are important in kinetic mechanisms, yet the two species are sensitive to different UV wavelengths. Thus, although an NO_2 chemical actinometer may be useful for general checks of chamber light levels, it alone would not be sufficient for an overall calibration check.

To date, only a few ambient direct measurements of k_{NO_2} have been made in the atmosphere. More such measurements need to be taken in a comprehensive and systematic way to determine typical rate constant values in a variety of conditions and to provide data for comparison to theoretical estimates. In this context, experimenters should record and publish the state of all parameters that can affect the actinic flux during their measurement periods. These include date and location, cloudiness, aerosol concentration or optical thickness (visibility is a useful surrogate), surface elevation, significant obstructions to the horizon, and the underlying surface. The actinometer should be located over a uniform underlying surface and should be distant from highly reflecting structures such as white walls. With such care in acquiring and reporting ambient measurements of photodissociation rate constants, the results of different experimenters can be compared along with theoretical estimates. Finally, we recommend that measurements be made of photodissociation rate constants vertically through the lowest several kilometers of the atmosphere, such as by mounting a chemical actinometer on an aircraft. More confidence could be placed on the theoretical computations of the vertical dependence of the rate constants described in this paper if they were experimentally verified.

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SESSION 16

MATHEMATICAL MODELS OF OZONE/OXIDANT AIR QUALITY - I

Chairman: K. Demerjian
Environmental Protection Agency

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PHOTOCHEMICAL AIR QUALITY SIMULATION MODELING: CURRENT STATUS AND FUTURE PROSPECTS

K. L. Demerjian*

ABSTRACT

Mathematical models that relate pollutant emissions to ambient air quality through the theoretical treatment of the chemical and physical processes of the atmosphere are reviewed. An evaluation of currently available models is presented and various shortcomings of state-of-the-art models are discussed. The St. Louis Regional Air Pollution Study model verification program is outlined and a discussion of the approach is presented.

INTRODUCTION

Pollutants emitted into the atmosphere as a result of man's activities are transported, dispersed, transformed, and deposited via complex physical and chemical processes. Mathematical models provide a unique technique for evaluating the impact of anthropogenic emissions on air quality and will prove to be formidable tools in implementing the mandates of the Clean Air Act. The purpose of this paper is to review and evaluate currently available photochemical air quality simulation models and to discuss their potential applications and future prospects.

The purposes for air quality simulation models and their ultimate potential applications are listed below:

- Research: Gaining an understanding of pollution processes on which to base air pollution abatement strategies.
- Environmental Legislation: Deciding what emission standards should be set for emissions from stationary, mobile, or indirect sources, in order to meet already agreed-upon ambient standards.
- Implementation Planning: Evaluating the effectiveness of emission control regulations in achieving ambient air quality standards.

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- Impact Assessment: Predicting the consequences of policy decisions in terms of resulting air quality.

- Source Identification: Determining which major sources most significantly deteriorate air quality in the modeled region.

- Monitor Siting: Evaluating optimum site selection for stations in an air monitoring network.

- Transportation and Land Use Planning: Determining the relative air quality effects of various alternatives for physical development.

- Episode Control System: Provide real-time simulation and control strategy capabilities for an alert warning system in order to avert episodes of extremely high pollutant concentrations.

Though some of these applications have been realized for inert species, primarily through the use of Gaussian plume models, complex numerical-atmospheric diffusion equation models have found limited application as a result of their complexity, extensive resource requirements, and most importantly, their unverified status. The issue of model verification and its role in the Regional Air Pollution Study (RAPS) in St. Louis is discussed later in this paper.

MODEL CLASSES, SCALES AND CHEMICAL MODES

Air quality simulation models (AQSM) fall into three broad meteorological classes. These are:

- Diagnostic - models which require input of predetermined meteorological data in time and space over the period of the simulation study.

- Prognostic - models which generate meteorological fields in time and space given initial and boundary conditions for the modeling domain.

- Climatic - models which utilize climatological data as input in developing meteorological fields for the AQSM.

AQSM scales, which range from micro to synoptic, have been broken into the four functional modeling domains below:

Local (micro)	(400 m X 400 m X 100 m)
Urban (meso)	(40 km X 40 km X H)
Regional (meso)	(800 km X 800 km X H)
Continental (meso-synoptic)	(2800 km X 2400 km X 2 km)

where H ≡ mixing height

The modeling domains outlined above could easily be expanded or contracted by a factor of two with little or no impact on the overall formulation of the model.

The chemical mode of an AQSM is either non-reactive or reactive. Non-reactive refers to those models that only consider inert pollutants or pollutants whose chemical transformation can be expressed by a first order reaction rate. Pollutants typically considered as non-reactive, as defined above, are total suspended particulates (TSP), sulfur dioxide (SO_2), carbon monoxide (CO), and sulfate ($SO_4^{=}$). Reactive models, the subject of this review, have been termed here as photochemical air quality simulation models (PAQSM). This is the result of the major role played by photolytic reactions in the atmospheric transformation processes of pollutant species. Pollutants typically considered in PAQSM include reactive hydrocarbons (HC), CO, nitric oxide (NO), nitrogen dioxide (NO_2), and ozone (O_3). Historically, the development of PAQSM has focused on the urban scale, where the ozone problem was thought to originate and reside. Recent field programs indicate that ozone and its precursors are not isolated to the confines of the urban complex, but are transported over scales of hundreds of kilometers and time periods of several days in many instances. Based on these findings, development work in regional scale photochemical air quality simulation models has begun.

MODEL FORMULATION

The development of a mathematical relationship for simulating the transport, dispersion, transformation, and disposition of pollutant emissions into the atmosphere can assume varied ranges of complexity depending on the application to be considered. Figure 1 gives some indication, conceptually, of the complex nature of the PAQSM and shows the interactions of the various physical and chemical processes operative in polluted atmospheres. Techniques available for treating transport and dispersion include gradient-transfer, Gaussian, similarity, and statistical approaches. Though each has been considered in atmospheric modeling, the Gaussian and gradient-transfer approaches have found the most prevalent use. In particular, PAQSMs have considered only gradient-transfer approaches, mainly due to the time-dependent nature of the chemical transformation processes.

The need for practical (operations oriented) PAQSM for describing the physical and chemical dynamics of the atmosphere has necessitated the development of simplified approaches in treating reactive species in the turbulent planetary boundary layer. This need for simplification has resulted in the use of the so-called atmospheric diffusion equation in PAQSM approaches (Equation 1).

$$\frac{\partial \bar{c}_i}{\partial t} + \bar{u}\frac{\partial \bar{c}_i}{\partial x} + \bar{v}\frac{\partial \bar{c}_i}{\partial y} + \bar{w}\frac{\partial \bar{c}_i}{\partial z} = \frac{\partial}{\partial x}\left(K_H \frac{\partial \bar{c}_i}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_H \frac{\partial \bar{c}_i}{\partial y}\right)$$

$$+ \frac{\partial}{\partial z}\left(K_V \frac{\partial \bar{c}_i}{\partial z}\right) + R_i\,(\bar{c}_i.....\bar{c}_n, T) + \bar{S}_i(x,y,z,t) \qquad (1)$$

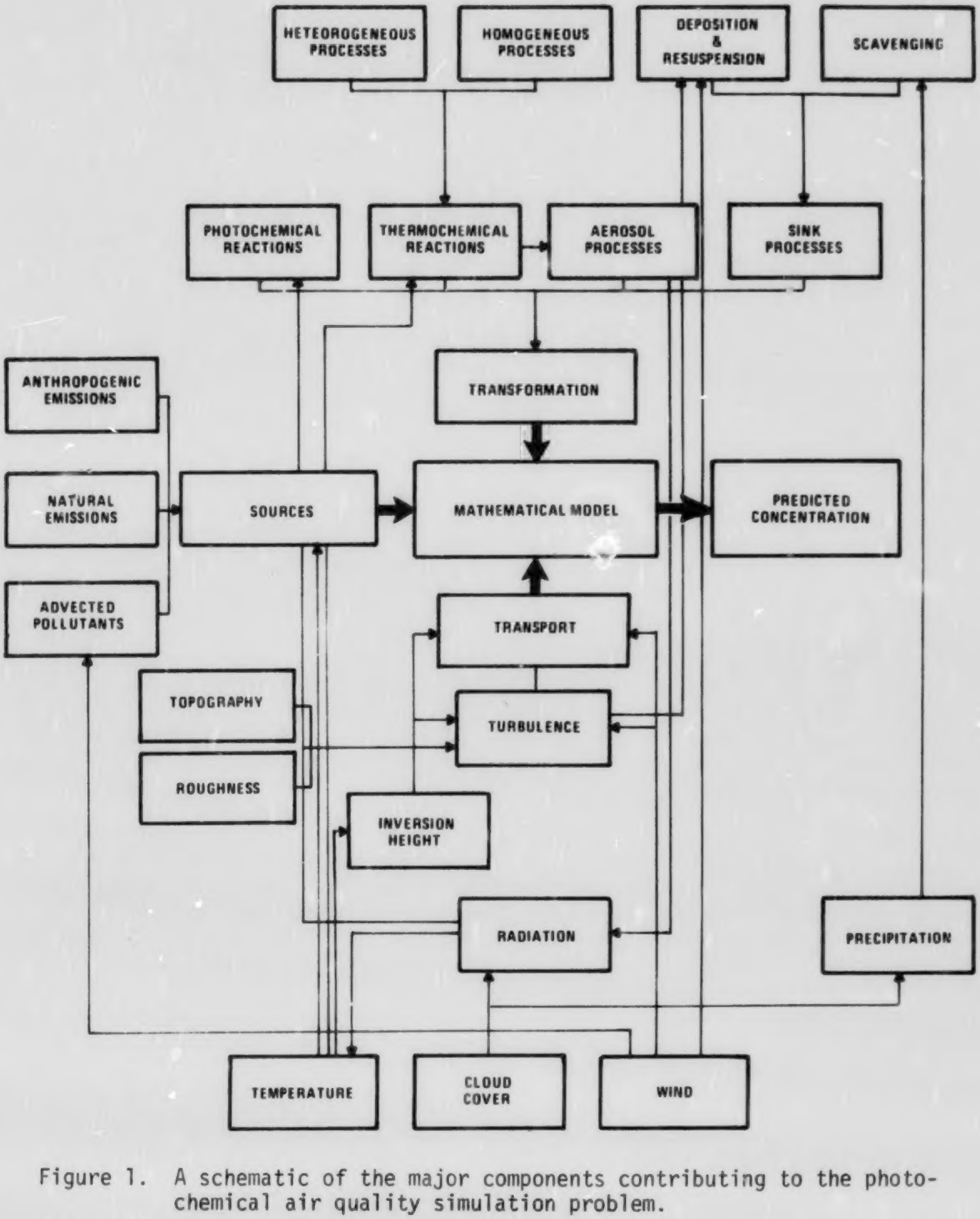

Figure 1. A schematic of the major components contributing to the photochemical air quality simulation problem.

where

$\overline{c}_i$ = ensemble mean concentration for species i

x,y,z= Cartesian coordinates

$\overline{u},\overline{v},\overline{w}$= ensemble mean velocities

K_H,K_V= horizontal and vertical eddy diffusivities

$\overline{S}_i$ = rate of injection (or removal) of species i by a source (or sink)

R_i = rate of production (or consumption) of species i through chemical

T = Temperature

t = time

The atmospheric diffusion equation is the result of the application of simplifying assumptions to the equation of conservation of mass. Since its derivation is given in many texts (for example, References 1,2), it will not be covered here, but some discussion of its entailing assumptions will be considered in the following section.

PAQSM CURRENT STATUS AND EVALUATION

A synopsis of currently available photochemical air quality simulation models is given in Table 1. The models covered are a representative sample of the scales and techniques currently available.

The evaluation of any air quality simulation model begins with assessing the validity of the basic assumptions used in deriving the models' working mathematical equations. In addition, identifying potential sources of error in various components used in the formulation of the transformation, emission, and transport modules of the PAQSM's is critical to evaluating the overall performance of models and in assessing potential sources for model inaccuracies. Seinfeld(2) and Demerjian(3) have recently reviewed this subject area and a summary of their respective findings is given in Table 2 and 3.

The sensitivity of a PAQSM to various errors associated with input parameters to the model has been reported by Liu et al.(11). A summary of the results, reported in Table 4, gives some insight into the potential inaccuracies that may be expected in PAQSM predictions. One cautionary note: the sensitivity study reflects only the response of the model to perturbations in its input parameters. No inference can be drawn between model sensitivity and that of the real atmosphere until verification studies confirm the soundness of the fundamental physical and chemical constructs of the model.

Initial and boundary conditions represent critical inputs to the PAQSM. In the case of the grid point approaches, boundary pollutant concentrations must be specified for each hour for all grid cells that lie along an inflow

TABLE 1. AIR QUALITY SIMULATION MODELS

Reference	Description & Basic Assumptions	Chemical Mode	Scale	Status
Reynolds et al[4-6]	Grid model based on numerical solution of the atmospheric diffusion equation. Numerical solution is based on the method of fractional steps. An explicit mass conservative scheme by Price, Varga and Warren is used in the horizontal and a Crank-Nicholson algorithm in the vertical. Wind field values are obtained from interpolation of ground level measurements using an inverse distance relationship or may be intirely user spedified.	Reactive - uses the Hecht-Seinfeld lumped reaction mechanism	Urban	Further development work underway, estimated completion early 1977.
Eschenroeder and Martinez[7]	Trajectory model based on a moving column of air in which vertical diffusion and chemical reactions take place. The column of air follows a surface trajectory interpolated from monitoring station wind readings.	Reactive - uses the Eschenroeder-Martinez lumped chemical kinetic mechanism	Urban	Further development work underway, estimated completion late 1977.
MacCracken and Sauter[8]	Multi-Box boundary layer model based on the numerical solution of the vertically integrated atmospheric diffusion equation, Gear's method is used in the numerical integration of coupled ordinary differential equations. The model utilizes a mass consistent wind field approach for generating detailed wind fields, vertical profiles of velocity and diffusivity.	Reactive - uses a generalized lumped kinetic mechanism developed at Lawrence Livermore Laboratory.	Urban	Further development work underway, estimated completion early 1977.
Sklarew et al[9]	Grid model based on numerical solution of the atmospheric diffusion equation. Numerical solution for the transport and diffusion processes is based on the particle-in-cell method. The three-dimension wind field is computed from surface maps.	Reactive - uses the Eschenroeder-Martinez lumped chemical kinetic mechanism	Urban	Development Completed
Hanna[10]	Cell model based on the solution of the dynamic mass balance equations with intercell flows neglected, for an array of well-mixed cells. A single representative wind speed is estimated from available surface maps.	Reactive - uses the Friedlander-Seinfeld parametric chemical kinetic mechanism.	Urban	Development Completed

TABLE 2. ERRORS ASSOCIATED WITH THE USE OF THE ATMOSPHERIC DIFFUSION EQUATION

True form of the turbulent fluxes $\overline{u'c_i'}$, $\overline{v'c_i'}$, and $\overline{w'c_i'}$ is unknown

Turbulent fluctuating chemical reaction terms are neglected

Mean velocities $\bar{u}$, $\bar{v}$ and $\bar{w}$ used in solutions are not true ensemble means

Chemical reaction mechanism R_i does not accurately reflect those chemical processes occurring in the atmosphere

Solutions on grids must be spatial consistent with the wind and emission resolution

TABLE 3. SOURCES OF ERROR IN THE DEVELOPMENT OF TRANSFORMATION, EMISSION AND TRANSPORT MODULES FOR PAQSM

Transformation - Chemical Kinetic Mechanism

Smog Chamber Related Errors

Inadequate or no control and measurement of levels of H_2O in the chamber.

Impurities in background chamber air.

Inadequate or no measurements of the spectral distribution and intensity of the chamber irradiation system.

Inaccurate or ambiguous analytical methods.

Non-homogeneity due to inadequate stirring or poor chamber design.

Adsorption and desorption of reactants and products on chamber walls.

Chemical reactions occurring on chamber surfaces.

Inadequate control and measurement of chamber temperature.

Chemical Mechanistic Errors

Uncertainties in experimental determinations of specific reaction rate constants.

(continued)

TABLE 3. (continued)

Chemical Mechanistic Errors (continued)

Variations of rate constants with temperature either uncertain or unknown.

Inadequacies in lumping due to the non-representativeness of lumped class reactions relative to specific species within the class, e.g., reaction rates, products, and stoichiometric coefficients.

Inaccuracies in the mechanism due to insufficient verification studies.

Source Emissions

Inaccurate or no specification of source location.

Uncertainties in emission factors.

Inaccurate or no temporal resolution of emission.

Inadequate or no verification of emission methodologies.

Transport

Uncertainties in the measurement of wind speed and direction.

Inadequate or non-representative spacial measurements of wind speed and direction.

Uncertainties associated with wind field analysis techniques.

Inadequate or no spacial and temporal measurements of vertical temperature.

Inaccuracies in the specification of eddy diffusivities in time and space.

Inadequate or no spacial and temporal measurements of solar radiation.

boundary from the ground to the inversion base. The horizontal boundary conditions are established, when possible, using nearby monitoring data as a guide. When such information is unavailable, estimates used are made solely on a judgmental basis. Concentrations are assumed invariant in the Z direction for any given x, y and t. Initial concentrations are specified in each ground level grid cell by interpolation using the data collected at monitoring stations during the hour at which the model run is initiated. For trajectory approaches, only initial concentrations need to be specified. The usual

TABLE 4. A SUMMARY OF THE SENSITIVITY OF A GRID POINT MODEL TO VARIATIONS IN INPUT PARAMETERS

Input Parameter	Variation	Local Maximum Deviation*	
		CO ppm	O_3 pphm
Wind Direction	Station measurements randomly perturbed by 0 or ±22.5°	|1.75|	
	Values at each grid point randomly perturbed by 0 or ±22.5°	|2.81|	
Wind Speed	Station measurements randomly perturbed by 0 or ±1 mph	|1.24|	
	Values at each grid point randomly perturbed by 0 or ±1 mph	|1.73|	
	Station Measurements decreased by 50%	+5.3	+43.7
	Station Measurements decreased by 25%	+2.4	+24.5
	Station Measurements increased by 25%	-2.4	-19.6
	Station Measurements increased by 50%	-4.2	-34.5
Horizontal Diffusivity (base value 50 m^2/sec)	Decreased to 0	|0.04|	
	Increased to 500 m^2/sec	|0.3|	
Vertical Diffusivity (base value 5 m^2/sec)	Decreased to 0.5 m^2/sec	+5.8	+36.3
	Increased to 50 m^2/sec	-3.0	-16.0
Mixing Depths	Decreased by 25%	+2.6	+15.3
	Increased by 25%	-1.5	-8.5
Radiation Intensity	Decreased by 30%	0	-19.0
	Increased by 30%	0	+14.0
Emissions Rate	Decreased by 15%	-1.4	-6.3
	Increased by 15%	+1.3	+5.6

* Largest deviation from the base case at any of the N locations in the grid

approach is to initiate the trajectory in the vicinity of an air monitoring station and to use the observed measurements as initial concentrations in the trajectory cell.

To illustrate the importance of boundary concentrations on grid point model calculations, comparative simulations for Los Angeles on September 29, 1969 were made by first using the standard prescribed boundary concentrations and by then using a reduced set of nominal boundary concentrations. All other conditions remained the same. Ozone average concentration maps for the Los Angeles basin between the hours of 1:00 and 2:00 P.M. are shown in Figures 2 and 3 for the respective simulations. A comparison of the results shows that only minor differences are observed at the eastern and northern edges of the basin where the maxima occur, but significant differences are observed at the western and central portions of the basin. The overall effect of the reduced boundary conditions was to bring an additional 904 square miles of the Basin below the oxidant standard, which is equivalent to 237% improvement in oxidant air quality in the modeling region on an area basis.

The impact of initial conditions on the grid point approach is illustrated in Figure 4. In this case, in addition to the reduced boundary condition (as in Figure 3), initial conditions prescribed in the model base case run were reduced by 50 percent. A comparison of results in Figures 3 and 4 shows reduction in the predicted ozone levels at the northern and eastern edges of the basin (the meteorological conditions for this day are such that these are the only two areas where some portion of the early morning initial pollutant concentration has been retained) to be of the order of 20 - 30 percent.

The importance of initial conditions on ozone predictions using a trajectory model approach are illustrated in Figure 5. In this case, comparative trajectory simulations were run for Los Angeles on September 29, 1969 for the original initial concentrations prescribed for the cell and plus and minus 20% of those values. The results indicate an approximate equivalent percentage change in the ozone maximum by the model.

REGIONAL AIR POLLUTION STUDY: MODEL VERIFICATION

The St. Louis Regional Air Pollution Study (RAPS)(12) is a five-year field program sponsored by the EPA and initiated in 1972. Three major objectives sought by the program are:

- Develop, evaluate and verify air quality simulation models on an urban scale covering urban/rural stationary and mobile sources.
- Develop, evaluate and verify models of local-scale phenomena that complement urban-scale models.
- Archive all data collected under the program in the form of a readily retrievable data base to use in evaluating future air quality simulation models and effects models.

Model verification studies have been very limited in nature due to the lack of adequate air monitoring data bases against which to test models. This

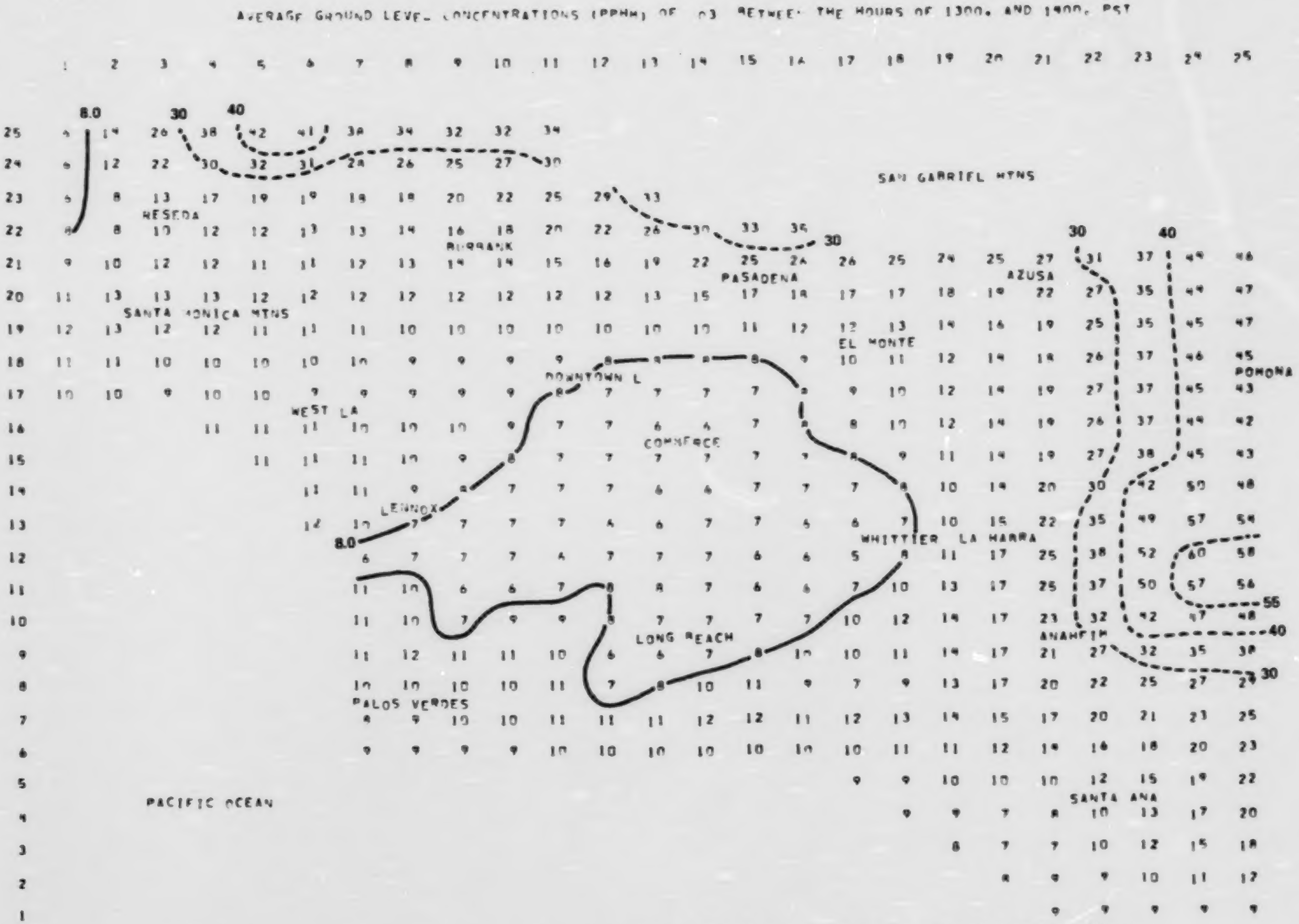

Figure 2. Predicted ozone concentrations in the Los Angeles basin September 29, 1969 using standard model boundary concentrations. (Systems Applications, Inc. Grid Point Model).

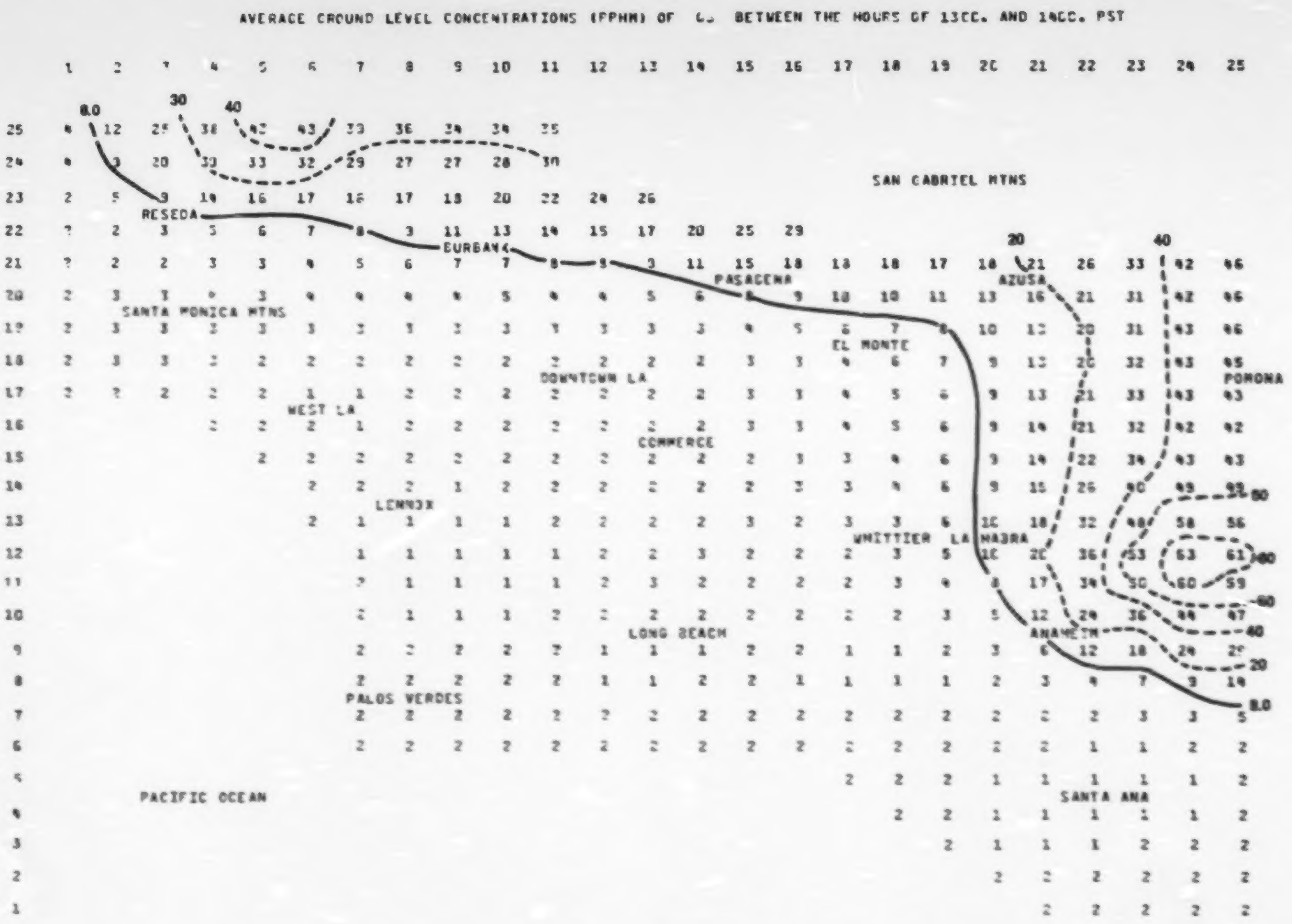

Figure 3. Predicted ozone concentration in the Los Angeles basin September 29, 1969 using reduced nominal boundary conditions. (Systems Applications, Inc. Grid Point Model).

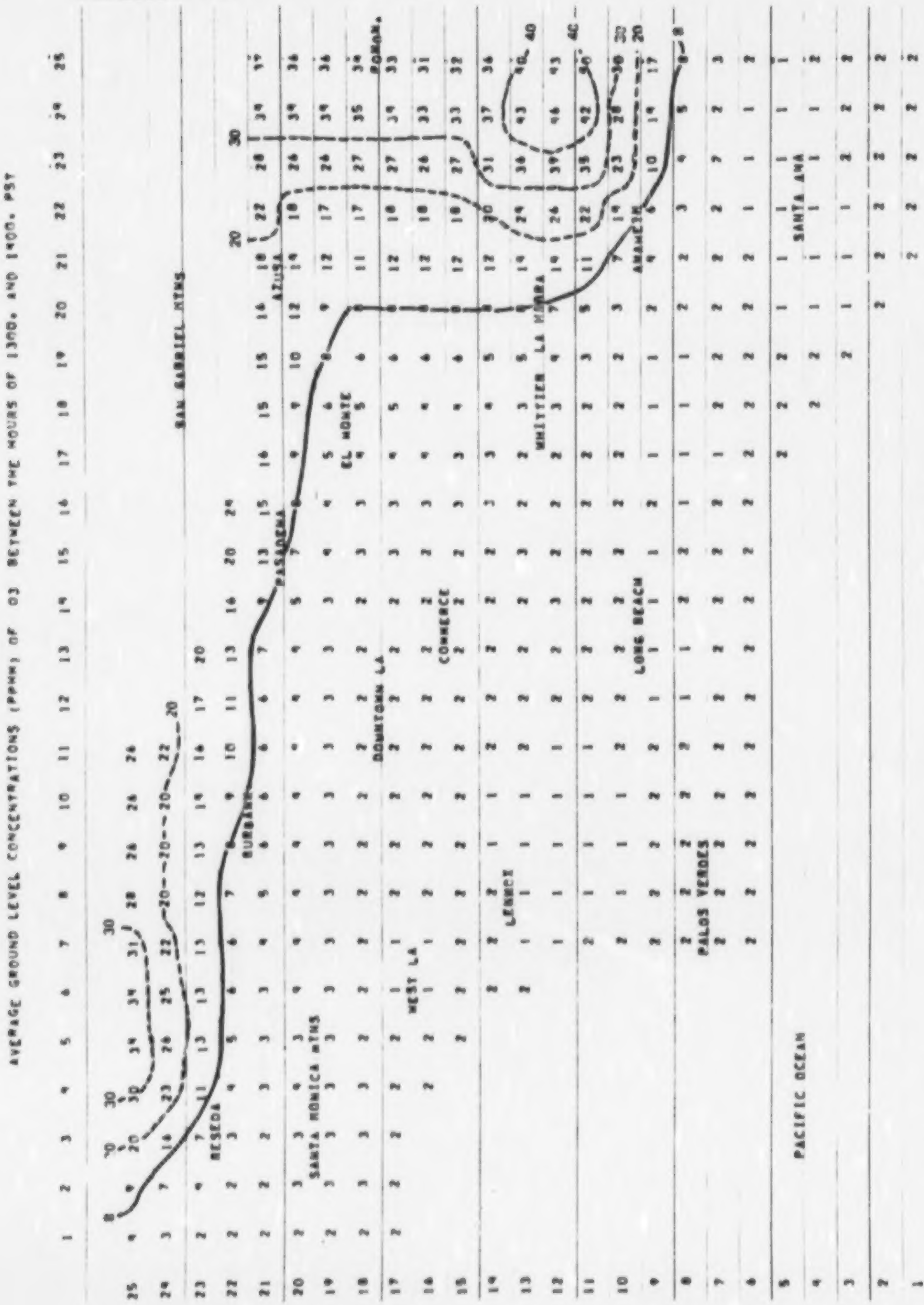

Figure 4. Predicted ozone concentrations in the Los Angeles basin September 29, 1969 using reduced nominal boundary conditions and initial conditions reduced by 50%. (Systems Application, Inc. Grid Point Model).

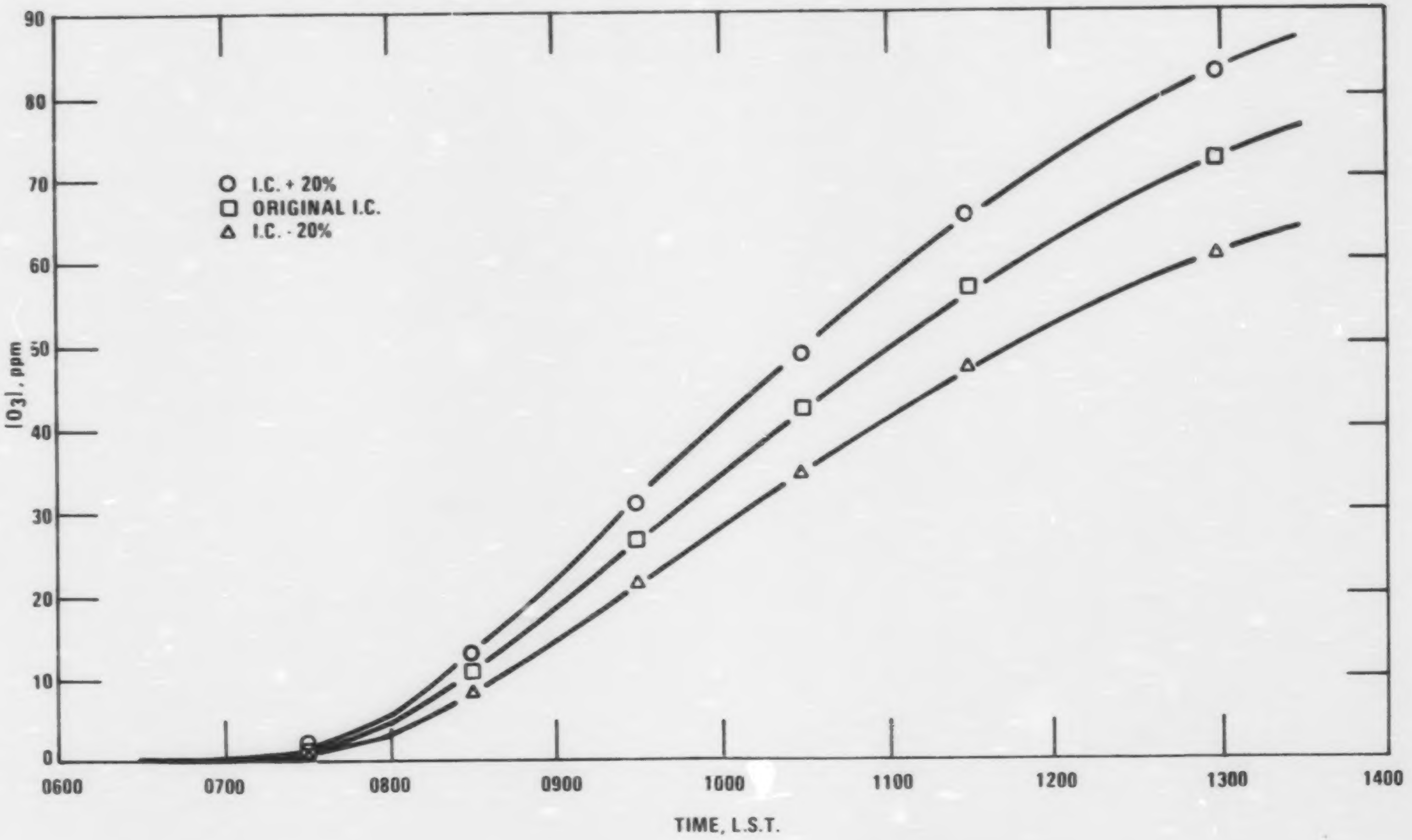

Figure 5. Predicted ozone concentrations in Los Angeles Basin September 29, 1969 using original and ±20% the initial concentration in the Trajectory Cell. (General Research Corp. Trajectory Model).

has proved to be a considerable deterrent in the application of the more complex models, due to their resource requirements and the unverified status of their results. The RAPS will provide the first adequate data set to allow model performance based on statistical criteria.

The monitoring network that came on line late in 1974 consists of twenty-five monitoring stations spatially distributed in a spiral configuration covering approximately a 6400 km^2 area. Routine chemical measurements include: O_3, NO, nitrogen oxides (NO_x), CO, methane (CH_4), total hydrocarbon, total sulfur, SO_2, hydrogen sulfide (H_2S), total suspended particulate and dichotomous particulate samples. Physical parameters measured on a routine basis include: wind speed and direction, temperature, dew point, vertical temperature gradient, pressure, solar radiation, and aerosol back scattering coefficient. Data tapes are routinely prepared based on one-minute and hourly averages of the measured parameters.

A schematic view of the elements of the RAPS air quality simulation model verification program is given in Figure 6. Since the verification of each and every urban-scale air quality simulation model currently in existence is an unrealistic task, the decision was made to select judiciously from the modeling stockpile a representative sampling of modeling techniques. The selected models will be then adapted to the St. Louis region and three test days will be considered for model debugging and tuning. Models will then be turned over to the Agency for the verification study.

The selection of days from the RAPS data base to form a subset of verification days to perform the studies will be done via a series of filtering programs. The filtering criteria may include such tests as:

- days in which criteria pollutant X had Y% or greater valid data,
- days in which criteria pollutant X exceeded an hourly average value of Y ppm;
- days in which criteria pollutant X exceeded a 24 hour average value of Y ppm.

The specific numbers to be used by the filters are currently being developed. The subset of verification days will then be stratified by season. Non-reactive models will be tested against randomly selected days within each season. An attempt will be made to distribute the verification test days proportionately among the four seasons. The reactive models will use randomly selected days, but in a disproportionate manner with respect to season. The larger sample selections will come from the summer months, and lesser sample selections will come from the spring, fall, and winter seasons.

After the selection of the model verification test days, a five-day subset will be chosen and input data to the models for those days prepared. The five-day subset will be used for preliminary testing and should allow spotting any major model inconsistencies. Any obvious minor model refinements at this stage will be considered. Since all the models selected will have undergone some form of evaluation and testing, major unresolvable inconsistencies are not ex-

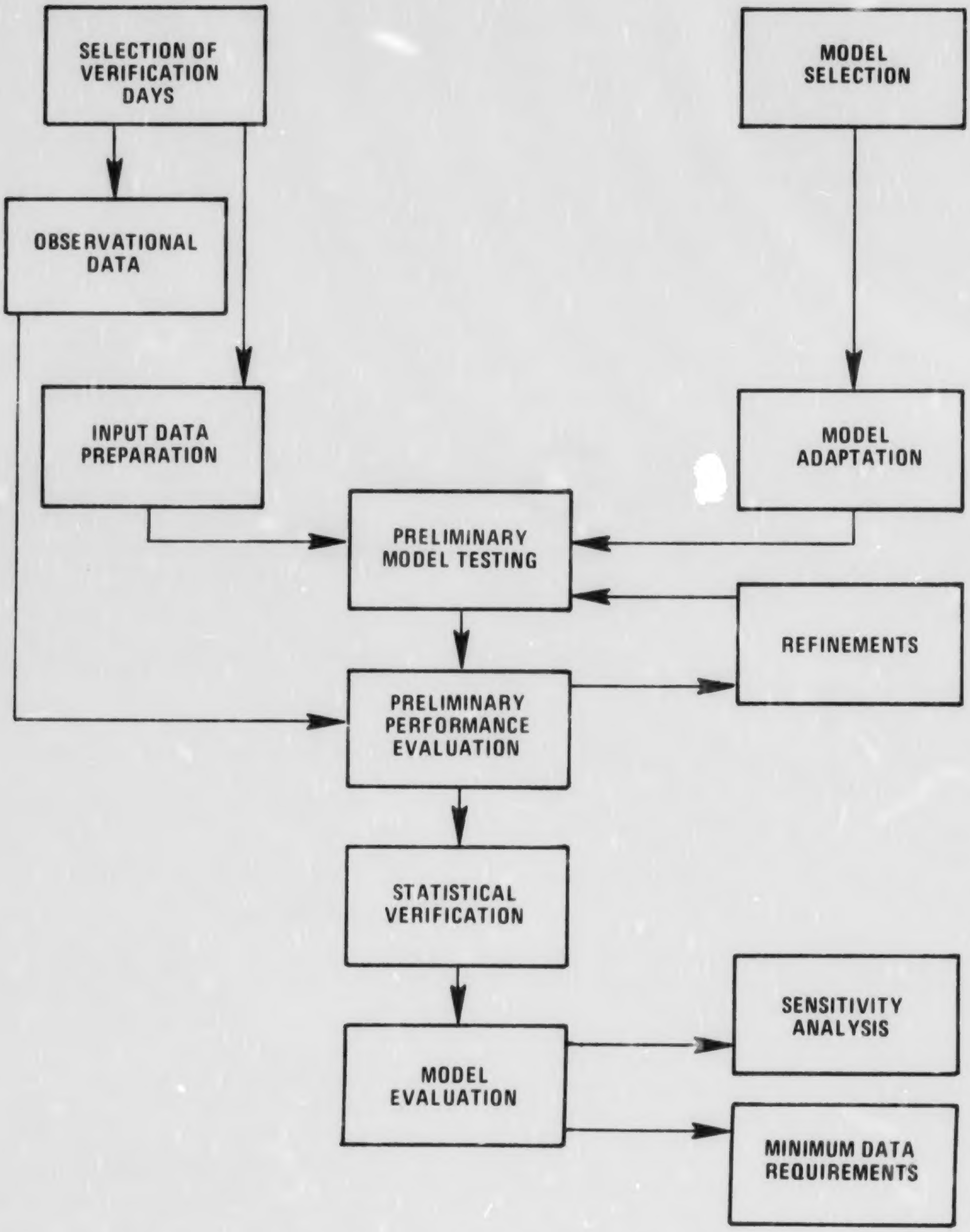

Figure 6. Elements of the RAPS Air Quality Simulation Model Verification Program.

pected. Should such a case arise, the verification studies for the particular model in question will stop and the preliminary test results will be sent to the model developer for study.

Once the preliminary model testing phase is completed, the statistical verification studies will begin. Approximately 50 computer simulation days will be considered for each model. Comparisons between computer predicted and observed hourly averaged concentrations of pollutants will be made on a day-by-day basis. Specific statistical tests for model verification studies have been discussed by Brier(13), Nappo(14), and Liu et al.(11). In light of these studies, several approaches are under consideration for the comparative studies. Model verification will provide the first adequate set of statistical criteria on which to judge model performance and will, in the final analysis, provide the necessary information for assessing and selecting models for various application purposes.

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THE SYSTEMS APPLICATIONS, INCORPORATED URBAN AIRSHED MODEL: AN OVERVIEW OF RECENT DEVELOPMENTAL WORK

S. D. Reynolds*

ABSTRACT

This paper summarizes work on photochemical model development carried out at Systems Applications, Incorporated over the past three years. As a result of this work, the original Systems Applications, Incorporated Urban Airshed Model has undergone significant modification and refinement. These refinements are discussed, and plans for assessing the accuracy of the model predictions are outlined.

INTRODUCTION

From 1970 to 1973, EPA funded a program at Systems Applications, Incorporated (SAI) that resulted in the formulation of a grid-based model capable of predicting the spatial and temporal behavior of ground-level concentrations of photochemical pollutants. To evaluate the performance of this model, we simulated six smoggy days that occurred during the fall of 1969. This work is discussed in detail in the reports by Roth et al. (1971) and Reynolds et al. (1973). Evaluation of the model's predictions and its components showed that improved treatments of some physical and chemical processes were necessary. This paper reviews the work that has been carried out at SAI since 1973 aimed at the development of a more accurate photochemical model.

In general, efforts to upgrade the SAI model have resulted in:

- The implementation of improved treatments of atmospheric transport and chemical reaction processes.
- The development of microscale modeling capabilities.
- The parameterization and incorporation of pollutant uptake processes.
- The refinement of numerical integration procedures.
- The development of aerosol modeling capabilities.

Other SAI studies conducted under Environmental Protection Agency (EPA) support include an assessment of prior model evaluation experiments, an examination of model sensitivity to variations in input parameters, and an analysis of the validity of grid and trajectory modeling concepts (Liu et al., 1976). The following sections are devoted to discussions of the overall model formulation and the treatment of its components.

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GOVERNING EQUATIONS OF THE MODEL

The fundamental equation governing the concentration of each pollutant species is the so-called mass continuity equation. After carrying out several mathematical operations and invoking a number of assumptions, this equation can be written in the following form:

$$\frac{\partial\langle\tilde{C}_\ell\rangle}{\partial t} + \overline{U}_i \frac{\partial\langle\tilde{C}_\ell\rangle}{\partial x_i} = \frac{\partial}{\partial x_i} K_i \frac{\partial\langle\tilde{C}_\ell\rangle}{\partial x_i} + \tilde{S}_\ell + \langle\tilde{R}_\ell\rangle + \langle\tilde{R}'_\ell\rangle + \langle\tilde{R}''_\ell\rangle, \qquad (1)$$

where the symbols < > and ~ represent ensemble and spatial averaging operations, respectively, and

C_ℓ = the approximate value of the instantaneous concentration of pollutant ℓ at a point*

$\overline{U}_i$ = mean wind velocity components

K_i = eddy diffusivity components

S_ℓ = rate of emission of pollutant ℓ from elevated sources

R_ℓ = contribution of the mean concentrations to the net reaction rate of pollutant ℓ

R'_ℓ = contribution of the turbulent concentration fluctuations to the net reaction rate

R''_ℓ = contribution of subgrid-scale concentration variations to the net reaction rate.

Ground-level emissions and pollutant uptake processes are treated in the boundary conditions.

Because the governing equations are nonlinear, they must be solved numerically. Furthermore, the use of numerical techniques generally requires that the modeling region be subdivided into an array of three-dimensional grid cells, where each cell may have horizontal and vertical dimensions on the order of a few kilometers and several tens of meters, respectively. Before the general mass continuity equation can be solved, it must be "filtered" to remove all small scale variations that the grid cannot resolve, both in the concentration field and in the independent parameters, such as K_i and $\overline{U}_i$. The necessary filtering can be accomplished by averaging the continuity equation at each point over a volume equivalent to that of a grid cell. This spatial averaging is denoted by the symbol ~ in Equation 1. In addition, Equation 1 has been time-averaged over an interval equivalent to that used in each step of the numerical solution procedure. Thus, the concentration predictions obtained from a grid model represent spatially- and time-averaged quantities.

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*Because a number of assumptions have been made in the derivation of Equation 1, it is only a model of the "true" equation. We wish to emphasize its approximate nature.

To clarify the origins of the three reaction terms, we note that they might typically be of the form:

$$<\tilde{R}_\ell> = -k<\tilde{C}_\ell><\tilde{C}_m>$$

$$<R'> = -k<C'_\ell \; C'_m>$$

$$\tilde{R}''_\ell = -kC''_\ell \; C''_m$$

where k is a reaction rate constant. The concentration fluctuations, C'_ℓ and C''_ℓ are defined by:

$$C'_\ell =<C -<C_\ell>$$

$$C''_\ell =<C_\ell> -<\tilde{C}_\ell>$$

C'_ℓ represents the turbulent concentration fluctuation, and C''_ℓ represents a fluctuation introduced by the spatial averaging of the continuity equation. The term $\tilde{R}''_\ell$ would be expected to be important only near large point and line sources where the "point" values of the concentrations are significantly different from the spatially averaged values. A more detailed derivation of Equation 1 is presented by Lamb (1976a).

The SAI Urban Airshed Model is fully three-dimensional and includes provisions for simulating 13 pollutants nitric oxide (NO), nitrogen dioxide (NO_2), ozone (O_3), nitrous acid (HNO_2), hydrogen peroxide (H_2O_2), paraffins, olefins, aromatics, aldehydes, peroxyacetyl nitrate (PAN), sulfur dioxide (SO_2), carbon monoxide (CO), and total aerosol mass concentration.* The vertical extent of the modeling region is selected by the user, although provisions have been made to facilitate the treatment of a mixing layer capped by a stable inversion layer. Both layers are important in multiple day simulations. At the present time, the computer codes can handle a 25 x 25 x 10 grid.

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*The aerosol component includes primary particulates and secondary organic, nitrate, and sulfate aerosols.

COMPONENTS OF THE MODEL

CHEMISTRY

A chemical kinetic mechanism is one of the most important components of a model for predicting concentrations of photochemical pollutants. A 31-step mechanism, called the carbon-bond mechanism, has been developed at SAI by Whitten and Hogo (1976) and adapted for use in the Urban Airshed Model.

Because of the association of reactions and reactivities with carbon bonds, the range of reactions and the range of rate constants in a kinetic mechanism can be narrowed considerably when each atom is treated according to its bond type. This concept is the basis for the carbon-bond mechanism. In this mechanism, hydrocarbons are divided into four groups: single-bonded carbon atoms, fast double bonds (i.e., relatively reactive double bonds), slow double bonds, and carbonyl bonds. Single-bonded carbon includes not only paraffin molecules, but also the single-bonded carbon atoms of olefins, aromatics, and aldehydes. Double bonds are treated as a pair of carbon atoms. An activated aromatic ring is considered as three double bonds in the present formulation of the mechanism, and because of a similarity in reactivities, aromatics are lumped with the slow (ethylene) double bonds rather than with the fast double bonds. The carbon-bond mechanism has been applied to available smog chamber data for propylene/NO_x, 1-butene/NO_x, butane/NO_x, propylene/butane/NO_x, and toluene/NO_x systems by shitten and Hogo (1976). Test results indicate that this mechanism performs significantly better than those previously employed in the Urban Airshed Model.

Also included in the mechanism are five reaction steps describing SO_2 oxidation and two reaction steps accounting for the formation of organic and nitrate aerosol products. Sulfate aerosol products are assumed to form as a result of the gas phase reactions leading to the production of sulfur trioxide (SO_3), which rapidly combines with water to give sulfuric acid (H_2SO_4). We have assumed that the ozone-olefin reaction is the limiting step in the production of organic aerosol, and that only olefins with at least six carbon atoms participate significantly in this process. Nitrate aerosol production is assumed to be proportional to the NO_2 concentration. Further details of the treatment of chemistry in the Urban Airshed Model may be found in the report by Reynolds et al. (1976b).

ADVECTION

In the original version of the Urban Airshed Model, the horizontal wind components were assumed to be invariant with height. Sensitivity studies reported by Reynolds et al. (1976a) indicate that inclusion of wind shear effects in the model can alter NO_2 and O_3 predictions significantly. Consequently, we expanded the capabilities of the model to treat wind shear phenomena.

Theoretical wind shear relationships were derived by Lamb (1976a) using the predictions of a planetary boundary layer model developed by Deardorff (1970). These relationships will be useful in instances when wind measurements aloft are not available. For situations in which wind measurements are available both at the surface and aloft, we developed an objective technique for preparing appropriate three-dimensional wind inputs to the model. [See Reynolds et al. (1976b)]. This technique is unique in that it incorporated provisions for treating perturbations to the flow field caused by thermal effects.

TURBULENT DIFFUSION

Eddy diffusivity coefficients have been derived through use of a novel methodology developed by Lamb (1976a). In this procedure, a point source is assumed to emit an inert pollutant into a turbulent boundary layer. Employing flow fields predicted by the model of Deardorff (1970), particles are released from a point and followed as they are transported downwind. From the particle trajectories, it is possible to calculate the pollutant concentration field downwind of the release point. Given the concentration and mean flow fields, we "invert" the mass continuity equation and solve for the diffusivity profile through use of optimal control theory techniques. Preliminary diffusivity results are reported by Lamb (1976a) and the final relationships incorporated in the Urban Airshed Model by Lamb (1976b).

OTHER MICROSCALE PHENOMENA

The diffusivity work cited above is but one example of a group of studies dealing with the treatment of phenomena that have characteristic spatial or temporal scales too small to be resolvable in an explicit, deterministic manner in urban-scale models. The two primary objectives of our microscale work have been (a) to identify and parameterize microscale effects that influence the spatially-averaged pollutant concentration field (such as that predicted by a grid model) and (b) to develop means for predicting the distribution of pollutants in the immediate vicinity of point and line sources. In order to make significant headway in this area, it was first necessary to develop an appropriate mathematical framework for treating microscale phenomena. This framework is described by Lamb (1976a).

To achieve the objectives cited above, we developed three microscale modules for use in the Urban Airshed Model. A point-source module treats the effects of plume rise, the influence of turbulence on chemical reactions in plumes (i.e., $\langle R'_\ell \rangle$), and subgrid-scale concentration variations and their influence on the overall net reaction rate in each grid cell (i.e., $\langle \tilde{R}''_\ell \rangle$). Moreover, this module can be used to estimate the "point" value of the pollutant concentration field downwind of a point source. The second module treats the subgrid-scale chemistry effects resulting from the emissions of a network of line sources in the groundlevel grid cells. In this layer of cells, taken to be about 20 meters deep, NO emissions from a roadway are allowed to react only with O_3 in the immediate vicinity of the roadway. The third microscale module estimates the concentrations of photochemical pollutants along highways and in street canyons. In this module, consideration is given to upwind pollutant concentrations, vehicular emissions, turbulent wake effects, chemistry, transport, and the design of the roadway (elevated, at-grade, or depressed). A more detailed description of these modules is given by Lamb (1976b).

SURFACE REMOVAL PROCESSES

A methodology for calculating the removal of gaseous pollutants by surface sinks was incorporated in the Urban Airshed Model. Surface removal was assumed to take place in two steps — transport to the surface followed by adsorption on the surface. Parameterization of this two step process was accomplished by defining a resistance to mass transport (the reciprocal of the tranport velocity) and a resistance to surface removal (the reciprocal of the deposition velocity measured under conditions when transport is not a limiting factor). The transport resistance is estimated from the theory of turbulent transfer in the atmospheric boundary layer, and the surface resistance is obtained from experimental data on the uptake of pollutants by various types of surfaces.

Although deposition rates of SO_2 have been measured under a relatively wide range of conditions, only a few types of surfaces have been examined. For other pollutants, few measurements are available. For the present, we made crude estimates of the uptake resistances of typical urban surfaces for all pollutants. Model sensitivity studies based on these estimates indicate that surface removal processes may have significant effects on the predicted concentrations of SO_2, NO_2, and O_3. This work is reported by Reynolds et al. (1976b).

NUMERICAL INTEGRATION METHOD

Refinements to the numerical integration method used to solve the governing equations have focused on the implementation of a more accurate technique for computing horizontal transport. Tests of a number of techniques by Reynolds et al. (1976a) indicated that the SHASTA, Egan and Mahoney, and finite element methods all offered the promise of significantly suppressing the propagation of numerical errors that typically plague grid models.

In making the final selection of a method to be included in the Urban Airshed Model, the finite element method was abandoned because it could not be adapted to the solution of 13 coupled, nonlinear partial differential equations in three spatial dimensions without a rather large expenditure of effort to develop an appropriate computer code. Further testing and evaluation of the remaining methods by Reynolds et al. (1976b) resulted in the selection of the SHASTA method. Although the Egan and Mahoney method was somewhat more accurate, the SHASTA method was found to require significantly less computing time.

SUMMARY

Developmental work carried out during the past three years has resulted in significant refinements of many components of the SAI Urban Airshed Model.

At the present time there is a clear need to evaluate the accuracy of the model's predictive capabilities. To make this assessment, we are currently adapting the model for usage in St. Louis. An important element of this work will be the design of appropriate means to interface the model with the Regional Air Pollution Study (RAPS) data base. When this work is completed, it will be possible to perform extensive evaluative studies. In addition, the computer codes are being revised somewhat to make them more efficient and easier to implement on a variety of host computers. Documentation for the codes is also being prepared as an aid to the potential user of the new version of the Urban Airshed Model.

ACKNOWLEDGMENT

The following members of the SAI Environmental Studies Group have made significant contributions to the developmental work summarized in this paper: J. Ames, G. E. Anderson, D. R. Durran, T. A. Hecht, H. Hogo, T. N. Jerskey, J. P. Killus, R. G. Lamb, M. K. Liu, J. P. Meyers, P. M. Roth, D. C. Whitney, G. Z. Whitten, and M. A. Yocke. Funding for this work was provided by the Environmental Protection Agency (Contracts 68-02-1237 and 68-02-2216).

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SESSION 17

MATHEMATICAL MODELS OF OZONE/OXIDANT AIR QUALITY - II

Chairman: K. Demerjian
Environmental Protection Agency

A SURVEY OF APPLICATIONS OF PHOTOCHEMICAL MODELS

J. E. Summerhays*

ABSTRACT

Photochemical models of several types are identified and their applications are reviewed. The focus is on the various applications of the more sophisticated models, i.e., Difkin and the Systems Applications, Incorporated model. In particular, an emission reduction study by the author using the Systems Applications, Incorporated model is reviewed. This study suggests that hydrocarbon control (1) can have a dramatic effect in reducing ozone concentrations, (2) tends to delay the time of peak ozone concentration, and (3) moves the area of highest concentrations farther downwind.

INTRODUCTION

There is much yet to be learned about the chemical and meteorological processes involved in the production of tropospheric ozone (O_3). Nevertheless, numerous mathematical models that estimate O_3 concentrations have already been developed. Several of these models have been used in validation studies, i.e., studies comparing model estimates to observed concentrations. On the other hand, few of these models have been applied in studies assessing the impact of changes in hydrocarbon (HC) and nitrogen oxides (NO_X) emissions. This paper is intended as an overview of these applications, including an extensive review of an unpublished application by the author (1).

Two models in particular, the "SAI Model" (2) (developed by Systems Applications, Inc.) and Difkin (3) (developed by General Research Corp.) have been applied in a wide range of studies. These models fit into a sophisticated class of models called photochemical dispersion models, giving explicit consideration to the chemistry, advection, and diffusion of the pollutants in a photochemical system. Other photochemical dispersion models have been developed by Lawrence Livermore Labs (4), by Pacific Environmental Services (5), and by Systems, Science and Software (6).

Many simpler photochemical models have also been developed. These include three statistical models: (a) a rollback model, developed by John Trijonis (7), (b) a "repro-model" which is a statistical condensation of results using the SAI model, developed by Technology Services Corp. (TSC) (8), and (c) a statistically-derived short-term predictive model, developed by

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Tiao, Phadke and Box at the University of Wisconsin (9). Also, three photochemical box models have been developed: (a) several versions of Hanna and Gifford's box model that are adapted to consider photochemical pollutants (10, 11, 16), (b) a model developed by S. Hameed and others at NASA's Goddard Space Flight Center (12), and (c) a model being developed by Ken Demerjian (this model has not been described in the literature). A model that is difficult to categorize is the one developed by Chameides and Walker (13). This model is designed to estimate rural O_3 concentrations based solely on measured rural methane and NO_x concentrations, assuming no further dispersion. Two other models that have been used to estimate O_3 concentrations in a large number of studies are linear rollback (14) and Appendix J (15). However, these two models are simplified models and are not considered in this study.

Validation studies are also not considered in this paper. Nevertheless, the reader may wish to refer to validation studies in Los Angeles for the SAI model, Difkin, the Pacific Environmental Systems (PES) model, the Systems Science Software (SSS) model, and the Hanna-Gifford model, reported respectively in References 2, 3, 5, 6, and 10. Validation studies have also been conducted for Difkin and Hanna-Gifford in Denver (16), for Difkin in San Francisco (17), and for the Lawrence Livermore Lab model in San Francisco.

MODEL APPLICATIONS

Table 1 summarizes the applications that have been made of photochemical models. As may be seen from this table, the applications of Difkin are more numerous and variegated than the applications of any other model. One of the first studies conducted using Difkin (18) is a type of study that should be conducted with all photochemical models — estimating the impact of a general reduction of HC and NO_x emissions. The study conducting this analysis using Difkin also assessed the importance of the initial concentrations, i.e., the concentrations assumed at the beginning of the model run. This study showed a strong dependence of estimated O_3 concentrations on whether or not the initial concentrations were reduced, i.e., whether or not emissions reductions began prior to the beginning of the modeled time period. The trajectories were not long enough for O_3 concentrations to reach their potential peak values, but in any case, a comparison of highest values attained showed that a 30% general emissions reduction without any change in initial concentrations resulted in only a 16% reduction in estimated O_3 concentrations.

This study also found some interesting results from a study of various patterns of reducing HC and NO_x initial concentrations. Not unexpected was the result that reducing the HC/NO_x ratios reduced the estimated O_3 concentrations. However, in one case in which both HC and NO_x initial concentrations were reduced without changing their ratio, the estimated O_3 concentrations actually increased.

Hameed's box model was used to study the same strategies as modeled by General Research Corp (GRC) (12). His results were more like what would be expected: emissions reductions caused a reduction in O_3 concentrations similar to that found by GRC, but a reduction of initial concentrations caused a sizable decrease in O_3 concentrations.

TABLE 1. APPLICATIONS OF PHOTOCHEMICAL MODELS

Model Name or Developer	Applier of Model	Reference Number	Subject of Application
Difkin	GRC	18	4 different emission reduction strategies in Los Angeles and a few initial concentration reductions
S. Hameed	Hameed	12	The same 4 strategies as above
Difkin	SRI	17	1980 Concentrations in San Francisco
Difkin	GRC	19	"Cold Start" emissions
Difkin	GRC	20	Substituting electric cars for gasoline cars
Difkin	SRI	21	A Los Angeles emergency episode plan
Difkin	ERT	22	Non-conventional fuel recovery plants
Difkin	Caltrans	24(& 23)	A proposed freeway
Difkin	GRC	(23 only)	A refinery
Difkin	GRC	25(& 23)	Various growth rates in Santa Barbara
Lawrence Livermore	LLL	4	Various patterns of changes to emissions
SAI	EPA	1	Various emission reduction strategies for 6 days in Los Angeles
SAI	SAI	26	A proposed transportation control plan for Los Angeles
SAI	TSC	8	Developing a repro-model for 9/30/69 in Los Angeles
SAI	EPA	27	Various radiation levels

viously published, and so this study is discussed at some length. The results of the other two studies fit in well with the author's results.

In the first part of the study by Summerhays, the model was operated assuming no emission reductions for each of the six days for which sufficient data is available to run the model. These six days are all in the 1969 "smog season" in Los Angeles. Then the peak estimated O_3 concentration at each of fifteen sites was compared with the peak actually measured at each site.

Table 2 provides statistics showing this comparison separately for each day. Ideally, of course, one would find Y = 1.00 x + 0.0 with a correlation coefficient of 1.0. It will be noted that in some cases the model estimates quite accurately and in other cases the model does not estimate as accurately. It is interesting then to look at the wind pattern for each of these days. A typical pattern in the fall in Los Angeles is for a southwesterly seabreeze to develop during the day. The model seems to do better on days when this pattern occurs than when it does not. The findings discussed below are also typically best illustrated on those days when this typical pattern developed, although results on the other days do also support the findings. In any case, it is obviously wise to avoid basing studies solely on one day of meteorological conditions.

TABLE 2. CORRELATION STATISTICS BETWEEN PREDICTED AND OBSERVED OZONE PEAKS (in pphm)

Day	The Best Fit Line*	Correlation Coefficient
9/11	Y = .29 x + 9.96	.27
9/29	Y = 1.01 x + .35	.88**
9/30	Y = .68 x + 1.15	.71**
10/29	Y = 1.03 x + 2.27	.63**
10/30	Y = -.38 x + 13.29	-.26
11/4	Y = 1.22 x - 1.81	.48

*Y = Model Prediction, x = Observation
**Statistically significant at the .05 level

In the second part of the study by Summerhays, nine different strategies involving various combinations of HC and NO_x emission reductions were tested.

These results were then compared to the case with no emission reductions, i.e., the actual 1969 emissions. One of the interesting results of this study was that the first increment of HC control caused a more than proportional reduction in O_3 concentrations at "downwind stations" and very little effect at "upwind stations." Here downwind and upwind are relative to downtown Los Angeles, the center of most emissions in the Los Angeles area. Figure 1 shows the peak estimated O_3 for four strategies at twelve selected sites on September 29. It can be seen from this graph that, at the downwind stations, the initial 50% HC control causes generally in the range of 65 to 85% reductions in peak estimated O_3. Subsequent emission control then seems to reduce peak estimated O_3 concentrations by a proportion similar to the emission reduction. However, estimated O_3 concentrations at the upwind stations seem to be unaffected by even the most stringent emission reduction strategies, implying that this O_3 was primarily advected from the region upwind of the airshed boundary.

In contrast to the situation for HC, control of NO_x had very little impact on O_3 levels. Figure 2, showing the impact of nine control strategies at five selected sites, demonstrates that NO_x control may cause either an increase or a decrease in estimated O_3 concentrations. In any case, the effect is relatively minor.

One of the main advantages of using a photochemical model to estimate the effect of changes in emissions is the ability to consider spatial and temporal variations both in the inputs and in the estimated concentrations. No changes were made to the spatial or temporal distribution of emissions in this study, but the emissions control caused some interesting changes in the temporal and spatial distribution of estimated O_3 concentrations. In particular, reductions in HC not only caused reductions in O_3 peaks but also delayed these peaks and caused a shift of the region of highest concentrations farther downwind. For September 29, when this effect was most marked, the peak at any one site typically occurred two hours later, and the peak concentrations were found over ten miles farther downwind after controls compared to before controls.

SUMMARY

This report has reviewed several interesting applications of photochemical models. The emission reduction studies using the SAI model, Difkin, and other models, and the variety of special studies using Difkin, all serve to illustrate the potential for the use of photochemical models for estimating the impact of changes in emission levels.

This report would not be complete, however, without emphasizing the developmental nature of photochemical modeling at this time. The SAI model, especially, has been undergoing extensive changes, including revamping the consideration of chemistry, and Difkin will be undergoing some of the same changes. In this context, it is important to remember that the studies summarized in this report demonstrate what the respective models find to be the effect of certain changes, not necessarily what would be found in the real world. Presumably as photochemical modeling is further researched, these models will have increasing reliability in simulating reality. As we seek to

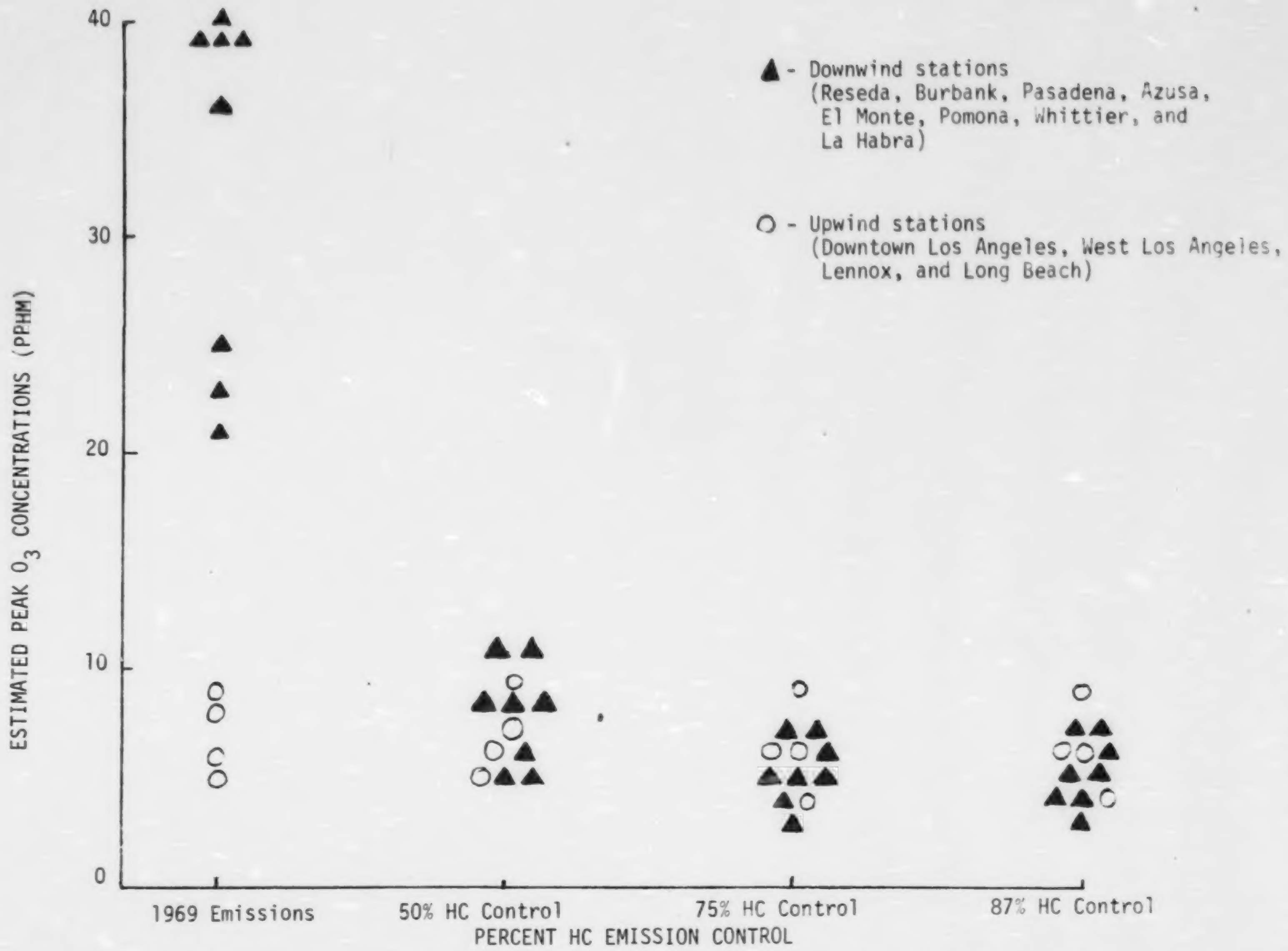

Figure 1. Comparison of estimated peak O_3 concentrations for September 29, 1969 and for three emissions control strategies: 50% NO_x and 50%, 75% and 87% HC control.

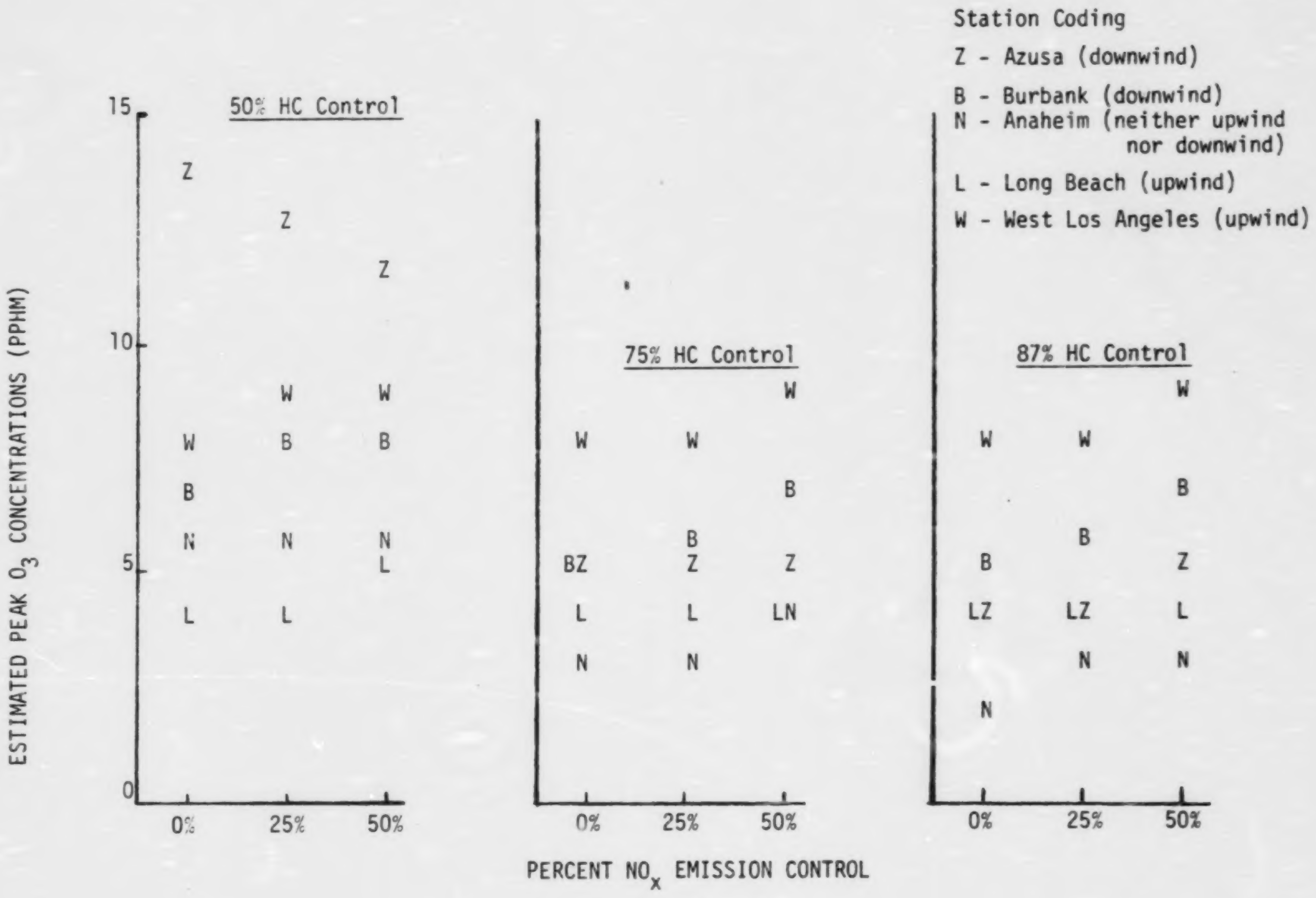

Figure 2. Three comparisons of estimated peak O_3 concentrations for various NO_x emission control strategies.

understand and solve our tropospheric O_3 problem, photochemical modeling should be an increasingly important tool to be used in achieving that goal.

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TESTS OF THE DIFKIN PHOTOCHEMICAL/DIFFUSION MODEL USING LOS ANGELES REACTIVE POLLUTANT PROGRAM DATA

G. H. Taylor and A. Q. Eschenroeder*

ABSTRACT

Using airborne and surface data obtained in the Los Angeles Reactive Pollutant Program conducted in the autumn of 1973, a series of trajectory simulations was carried out using the DIFKIN program (a semi-Lagrangian model utilizing chemical kinetics and K-theory diffusion calculations) as a preliminary step in modification of DIFKIN to embody recent updates in kinetics and diffusion theory. The trajectory of an air parcel was determined from Los Angeles Reactive Pollutant Program tetroon data, and pollutant fluxes were derived from emissions inventories for successive grid squares underlying the air parcel. Observed values of solar zenith angle, vertical eddy diffusivity, and initial pollutant profiles comprised the additional input parameters for the simulation. Integration was conducted every minute, and printed output was obtained for every 20-minute interval. Predicted concentrations at the various vertical levels were compared with helicopter and surface observations obtained in the Los Angeles Reactive Pollutant Program study. Similarities and differences were noted and discussed, and suggestions for improvements to be utilized in the forthcoming model were outlined.

DESCRIPTION OF THE MODEL AND THE DATA BASE

The Los Angeles Reactive Pollutant Program (LARPP), sponsored by the Coordinating Research Council, Inc., with cooperation from the Environmental Protection Agency (EPA), National Oceanics and Atmospheric Administration (NOAA), and California Air Resources Board (CARB), was aimed at supporting "the development of sound, unbiased scientific information relating to air pollution" (1). A total of 35 operations was conducted, with primary interest focused upon tracking and measurement of a moving air parcel within the marine layer for the purpose of providing a data base for air quality models. To accomplish this, constant-pressure balloons (tetroons) were tracked by radar; their positions were relayed to instrument-equipped helicopters and an air quality van, which attempted to follow the tetroons as closely as possible and, therefore, monitor the air parcel surrounding the tetroons. Careful planning and auditing were conducted in obtaining the experimental data; as a result, the completed data archives represent a well-documented source of information for pollutant analysis and model validation.

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In recent years, regulatory agencies have required the development of photochemical diffusion models dealing with both atmospheric chemistry and diffusion processes. The fact that all but a few of the regulated pollutants undergo atmospheric transformations requires that these more complex models supplant the diffusion models used previously. Only where chemical reactions are not significant in the determination of atmospheric concentrations can the simpler models (generally Gaussian in nature) be used with confidence.

Evolving during the middle and late 1960's, the DIFKIN model (a photochemical DIFfusion/KINetics program) was based on a Lagrangian approach involving air trajectories over the pollutant emissions sources. Preliminary analyses indicated excellent correlation between predicted and observed pollutant concentrations (2); nevertheless, certain aspects of the model have become outdated due to advances in chemical and diffusion theory. For that reason, scientists at Environmental Research and Technology, Inc. (ERT) have begun the process of writing a new program (under the acronym ARTSIM**) to entail recent technical improvements. In order to reassess the performance of DIFKIN using a complete, well-documented data base, LARPP data were utilized in setting up a series of simulation runs to recalibrate the model and delineate possible areas of improvement for use in ARTSIM development.

DIFKIN carries out three major functions: calculation of an air trajectory using wind data; determination of source emissions along the trajectory path; and the computation of concentrations of pollutants at times and for several vertical levels within the air parcel (3). Calculation of the trajectories was bypassed, and a trajectory determined by tetroon positions was input directly. Inputs necessary for the current study included surface pollutant fluxes, photochemical rate constants, vertical eddy diffusivities, and initial pollutant profiles.

Since DIFKIN calculations are based on a finite-difference solution to a K-theory diffusion equation with time- and height-dependent parameters, vertical eddy diffusivities must be input for several vertical levels and updated to account for changes in atmospheric structure. Diffusivities used in the current study were obtained using a procedure based on vertical variations in temperature and wind speed; the diffusivity values were updated hourly.

Surface emission fluxes were required for the primary pollutants nitric oxide (NO), carbon monoxide (CO) and reactive hydrocarbons (RHC), and were obtained from Reference 4; data consisted of stationary and mobile emissions. The mobile emissions were broken down into freeway and surface street emissions for each hour in 2x2 mile squares.

It is necessary to provide initial concentrations of six pollutants (NO, nitrogen dioxide (NO_2), RHC, CO, ozone (O_3), and nitrous acid (HNO_2) at five vertical stations (the levels used in this simulation were at the surface and 250, 500, 750, and 1000 meters above the surface)* as DIFKIN input. Surface concentrations were obtained from LARPP van data and 250 meter data were obtained from LARPP helicopters; initial concentrations at the remaining three levels were estimated from other available data (and generally were quite low). Adjustment of data became necessary in order to preserve the photostationary equilibrium set up by the following three reactions:

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*These elevations were established by the flight patterns adapted during the selected portions of Operation 33.

** Atmospheric Reaction and Transport SIMulation.

$$NO_2 + h\nu \rightarrow NO + O \qquad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3)$$

Since Equation 2 is known to be a very fast reaction, Equation 1 and Equation 2 are often combined into the single reaction

$$NO_2 + h\nu \rightarrow NO + O_3 \qquad (4)$$

Letting k_1 be the rate constant for Equation 4 (a function of solar zenith angle and, therefore, time-dependent) and k_3 the rate constant for Equation 3 (assumed to be constant with time), a photostationary balance has been postulated (5) between the three pollutants involved, such that

$$\frac{[O_3 \text{ pphm}] \cdot [NO \text{ pphm}]}{[NO_2 \text{ pphm}]} = \frac{k_1}{k_3} \qquad (5)$$

The above result is based on laboratory experiments of fully-mixed parcels. Since an air parcel in the atmosphere may be heterogeneous if mixing is inhibited (such as during more stable atmospheric conditions), and because local NO sources affect measurements, the observed ratio in Equation (5) may not correspond to the ratio of rate constants. During the present study, for example, the observed ratio derived from LARPP data was occasionally an order of magnitude larger than the k_1/k_3 values.

CASE STUDY: LARPP OPERATION 33, NOVEMBER 5, 1973

Of the 35 LARPP sampling days, Operation 33 was a particularly useful one, due to long duration (over 7 hours of helicopter flight time) and lack of logistics problems. A group of three tetroons was launched at 0715 PST from Downey, 17 kilometers southeast of central Los Angeles. Upon instructions from the radar operators, the LARPP helicopters were dispatched to locations of the tetroons, and flew four-leg square patterns at incremental altitudes. The patterns surrounded the centroid of the three tetroons.

Vertical temperature structure and wind speed data, necessary for calculation of vertical eddy diffusivities, were obtained from 0530 PST rawinsonde flights at El Monte (EMT) and Los Angeles International Airport (LAX), 1330 PST El Monte soundings, and from LARPP measurements. Table 1 is a list of diffusivities input for each necessary level at every hours. Since diffusivities are specified at only six vertical stations, it is usually necessary to interpolate the actual values to avoid aliasing problems.

In order to preserve photostationary state requirements outlined earlier, adjustments of initial pollutant concentration was necessary. The observed $[O_3][NO]/[NO_2]$ ratio was much higher than the k_1/k_3 value. Experimentation indicated that best results were obtained by decreasing the O_3 value and increasing NO_2, leaving NO as observed. Table 2 is a list of observed and corrected concentrations for the five vertical levels. k_1 values utilized as input parameters were obtained from Reference 6.

RESULTS

DIFKIN output consists of concentration profiles at five vertical levels (the same altitudes specified by the input concentrations) updated at a user-specified time interval (in this case 20 minutes). Surface concentrations of O_3, NO, NO_2, RHC and CO, as a function of time, appear in Figures 1a through 13; both predicted (DIFKIN) and observed (LARPP) concentrations are included. Figures 2a through 2e give concentrations for the same pollutants at the 250-meter level.

Since the observed concentration ratio appearing in Equation 5 was approximately an order of magnitude greater than that predicted by k_1/k_3, initial O_3 input was much smaller than measured values (0.3 pphm instead of 4 pphm), and NO_2 input was much larger (16 pphm instead of 7 pphm). As a result, O_3 predictions remain below observed values for approximately 3 hours, after which excellent correlation is found; NO_2 predictions, however, remain much higher than observations throughout the simulation (see Figures 1a and 1b). Nitric oxide values, which were not manipulated, are seen to correlate very well with measurements (Figure 1c). Quite clearly a problem in accuracy is inherent, due to the k_1/k_3 anomaly: successful simulation of O_3, NO and NO_2 will depend on the development of mixedness corrections for the rate constants. In the present case, two of the three were well accounted for (at least after 1000 PST); by changing the initial balance it may be possible to adjust the simulation to accurately assess any two of the three.

Regarding the airborne (250 meter) measurements, though an imbalance occurred similar to that outlined above, the difference between observed and adjusted initial concentrations was considerably less than that at the surface. Such behavior is to be expected since the degree of mixing at 250 meters above the surface is greater than that at the surface in the proximity of primary pollutant sources. After 1000 PST, for example, both O_3 and NO_2 predictions remained relatively close to observed values (Figures 2a and 2b), as in the ground level case; measured NO levels were closely approximated by the program (Figure 2c).

Carbon monoxide is a relatively nonreactive pollutant which can be utilized to assess the accuracy of diffusivity values and/or surface pollutant fluxes. As is evident in Figures 1e and 2e, DIFKIN predictions provide excellent approximations of measured concentrations throughout the morning hours, indicating that diffusivity and flux inputs are reasonable. Between 1200 and 1400 PST, the model overpredicts somewhat, indicating that assumed surface

TABLE 1. VERTICAL EDDY DIFFUSIVITIES USED IN DIFKIN SIMULATION (m^2/min)

HEIGHT ABOVE SURFACE (m)	TIME 0700	0800	0900	1000	1100	1200	1300	1400
0	126.0	126.0	330.0	348.0	348.0	360.0	360.0	360.0
125	72.0	72.0	76.8	590.0	666.0	720.0	720.0	720.0
375	69.0	69.0	69.0	69.0	186.0	306.0	306.0	306.0
625	42.6	42.6	42.6	42.6	42.6	42.6	42.6	42.6
875	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6
1000	27.0	27.0	27.0	27.0	27.0	27.0	27.0	27.0

TABLE 2. OBSERVED AND CORRECTED (FOR DIFKIN INPUT) VALUES OF O_3, NO, NO_2

HEIGHT ABOVE SURFACE (m)	OBSERVED CONCENTRATIONS (pphm)			RATIO $\frac{[O_3][NO]}{[NO_2]}$	ACTUAL $\frac{k_1}{k_3}$	CORRECTED CONCENTRATIONS (pphm)		
	O_3	NO	NO_2			O_3	NO	NO_2
0	4.0	20.0	10.0	8.0	.203	0.3	20.0	29.6
250	6.0	7.0	3.0	14.0	.203	1.0	7.0	34.5
500	--	--	--	--	.203	4.0	0.5	9.85
750	--	--	--	--	.203	4.0	0.5	9.85
1000	--	--	--	--	.203	4.0	0.5	9.85

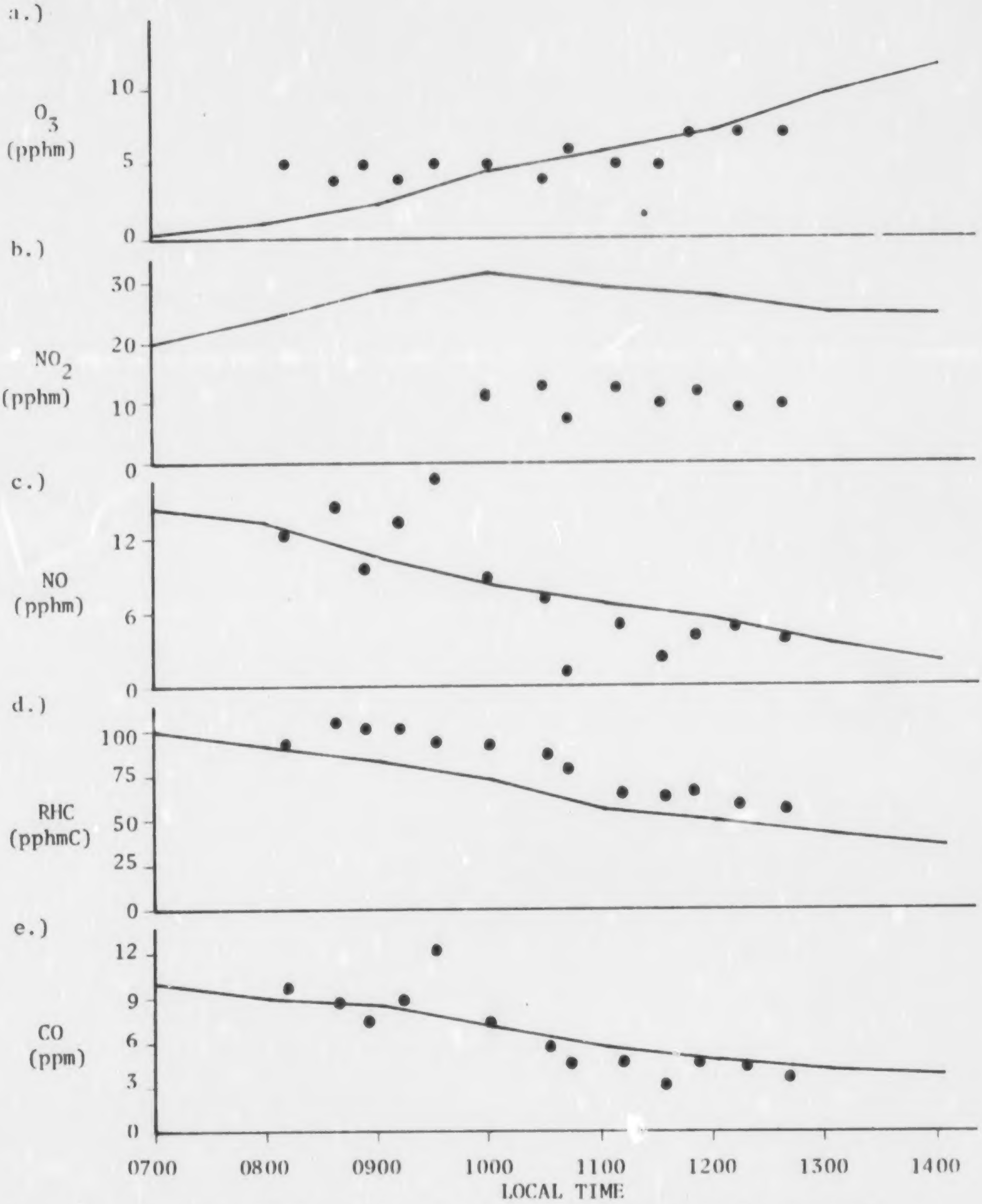

Figure 1. Surface DIFKIN predictions (solid lines) and LARPP observed concentrations (circles), November 5, 1973.

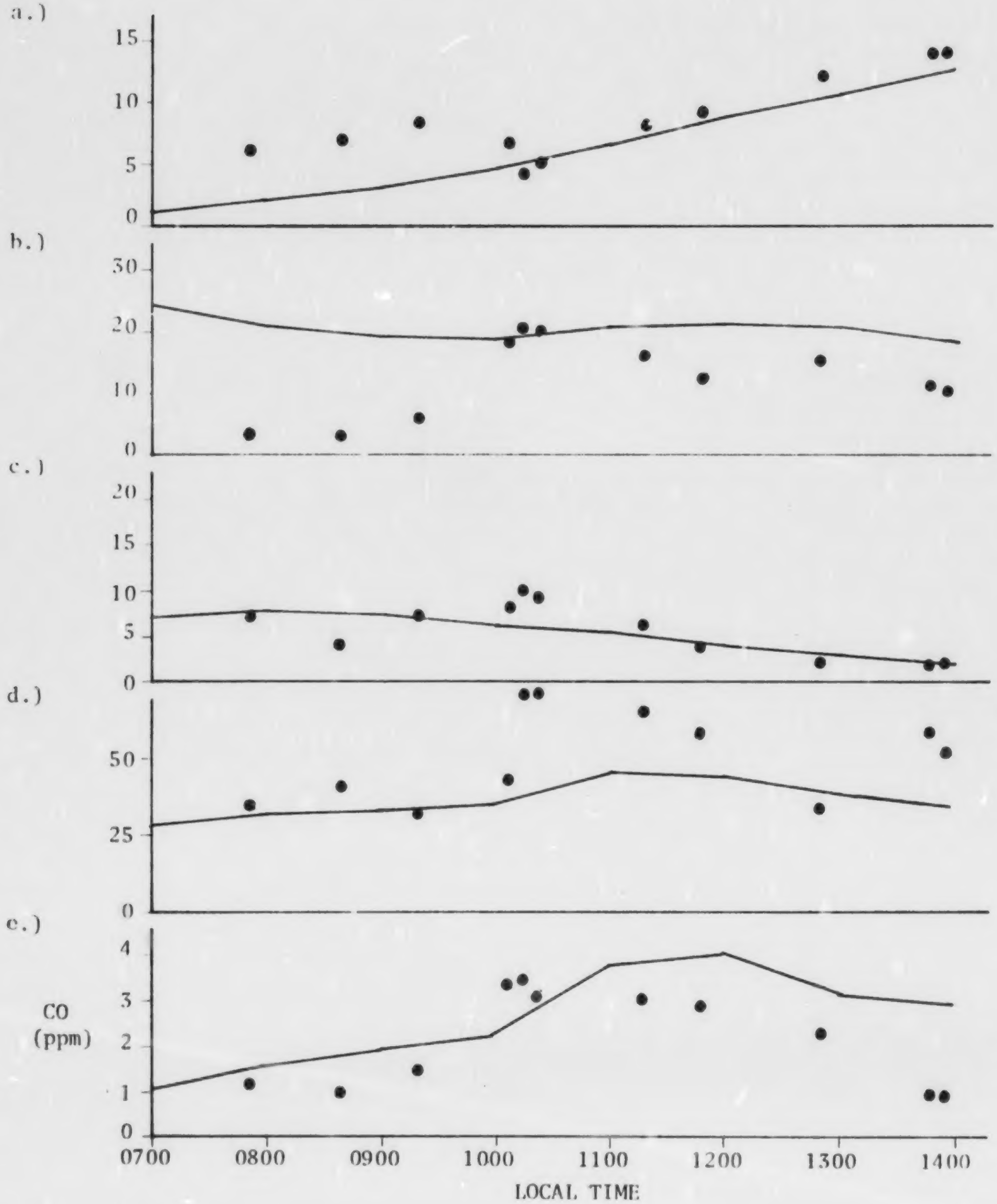

Figure 2. 250 m. DIFKIN predictions (solid lines) and LARPP observed concentrations (circles), November 5, 1973.

fluxes and/or upper-level (375 m) diffusivity values are excessive.

Although reactive hydrocarbon predictions agree quite well with 250 m measured data, surface observations are somewhat higher than the model output (see Figures 1d and 2d). Two possible explanations are offered: traffic levels may be slightly higher than assumed; and the measurement van, which operated on or near the surface streets, may be heavily influenced by microscale "puffs" of emissions which exceed ambient levels. Both occurrences are difficult to assess or rectify; it may be necessary to apply a correction factor to predictions to account for this anomaly.

CONCLUSIONS

The chief factor impeding accurate air pollutant predictions using the DIFKIN model appears to be the $NO-O_3-NO_2$ balance represented in Equation 5. Since experimental results assume (and utilize) a well-mixed atmosphere, actual measurements during more stable conditions (generally night and morning hours) can yield balances which differ greatly from experiment. It would be highly desirable to establish a prediction scheme for the pollutant balance as a function of stability and height, perhaps for incorporation into the ARTSIM development. The ratio in Equation 5 is highly dependent on the degree of homogeneity of the pollutant mixture. A physically-based empirical correction depending on source emission configurations and atmospheric turbulence will be necessary to rectify this problem.

Although the well-known problems of emission source inventory accuracy, diffusivity accuracy, and realism in the kinetic model still provide a challenge, this test of a photochemical diffusion model against three-dimensional atmospheric data has provided encouraging insights into the directions of model improvement. The expanded data base provided by the LARPP study is certain to provide further guidance in the development of air quality simulation models.

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DEVELOPMENT OF A MARKOV CHAIN MODEL FOR PHOTOCHEMICAL OXIDANT PREDICTION

J. R. Martinez*

ABSTRACT

A method is described whereby the time series of hourly photochemical oxidant is modeled by a Markov chain. The Markovian structure of the time series is tested using data for Houston, Texas. The output of the Markov model is shown to be related to the statistical criterion imposed by the National Ambient Air Quality Standard for photochemical oxidants. A technique to estimate the parameters of the Markov chain is briefly discussed.

INTRODUCTION

The National Ambient Air Quality Standard (NAAQS) for photochemical oxidant is based on a probabilistic criterion that requires that the hourly average concentration of 0.08 ppm not be exceeded more than once a year. Expressed in terms of probabilities, the NAAQS imposes that

$$\text{Prob}(\chi > 0.08) \leq 1/8767$$

where χ is the hourly average oxidant, Prob ($\chi > 0.08$) denotes the probability of χ exceeding 0.08 ppm, and 8760 is the number of hours in a (non-leap) year. In view of this requirement, it would be helpful to those involved in air quality management to be able to predict the probability of exceeding the 0.08 ppm threshold in a specified area over a one-year period. This would enable one to estimate whether the NAAQS would be met in the future.

This report describes progress toward the development of a model of photochemical oxidant using a Markov chain. The model's output is the probability of exceeding 0.08 ppm during a year in a given geographical region. The forecast of such statistical data complements results of other models which predict absolute concentration levels.

In developing the Markovian model we seek answers to several questions, namely:

- How is the Markov chain defined?
- Does the time series of oxidant values satisfy the Markovian assumption?

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- How can one predict the values of the parameters of the Markov chain?

In the sequel we attempt to provide answers to these questions. Specific examples using data for Houston, Texas are provided.

MODEL FORMULATION

DEFINITION OF STATES

The motivation behind the Markov chain approach stems from the fact that the NAAQS for oxidant basically distinguishes between two mutually exclusive conditions or states as regards air quality. One condition occurs when the hourly oxidant level exceeds 0.08 ppm; the complementary condition occurs when oxidant concentrations are at or below 0.08 ppm. Consequently, it is natural to think in terms of a two-state system where one state denotes exceedence of the .08 ppm threshold and the other state denotes nonexceedence. More formally, let s(n) denote the state of the atmosphere at the nth hours. Then we define two states, denoted by 0 and 1, as follows:

$$\begin{aligned} s(n) &= 0 \text{ if } x_n \leq 0.08 \text{ ppm}, \\ s(n) &= 1 \text{ if } x_n > 0.08 \text{ ppm}, \end{aligned} \tag{1}$$

where x_n is the average oxidant concentration at the nth hours.

Note that state 1 represents the occurrence of oxidant concentrations which exceed the 0.08 ppm threshold specified by the NAAQS. Thus, the NAAQS is not satisfied if in a one-year period the probability of state 1 occurring is greater than 1/870. The output of the Markov chain model consists of the probability of occurrence of state 1, thereby providing a direct indication of the degree of compliance with the NAAQS.

THE MARKOVIAN ASSUMPTION

The assumption which forms the basis of the Markov chain is that the occurrence of a state at time (n + 1) depends solely on the state of the system at time n. The states of the system at times earlier than n are assumed not to influence the state of time (n + 1). This is a very strong assumption which is not always satisfied since a system's memory may extend over more than one time interval. In our application to photochemical oxidant, we must test the autocorrelation function of the oxidant time series to determine the degree of dependence between states at successive times. Such analysis has been carried out for Houston and the results are shown in Table 1. It is apparent from Table 1 that the 1-hour dependence is strong. As might be expected, the dependence decreases as the time lag increases. The magnitude of the autocorrelation for a 1-hour time lag provides evidence for considering the oxidant time series as a sequence of dependent events which can be approximated by a Markov chain. Other tests have been performed which bolster the use of the Markovian approximation (1).

TABLE 1. AUTOCORRELATION FUNCTION OF OXIDANT TIME SERIES FOR HOUSTON AT MAE DRIVE, MAY-SEPT. 1973-1974, 0800-1900

TIME LAG (HOURS)	1973	1974
1	.7	.7
2	.5	.4
3	.3	.3

For completeness, at this point we should mention that in Houston most of the exceedences of the 0.08 ppm level occur during the months of May through September, always between the hours of 0800 and 1900.

OUTPUT OF MARKOVIAN MODEL

In accordance with the mandates of the NAAQS, we are interested in finding the probability of state 1 occurring over a large number of transitions. This is termed the limiting state probability and is found by using standard methods described in References 2 and 3. The limiting probability of state 1 will be denoted by Π_1. Once obtained, one checks whether $\Pi_1 \leq 1/8760$, thereby assessing whether or not the NAAQS is satisfied and, if not, how far the region is from being in compliance with the standard.

MODEL PARAMETERS

The behavior of the Markov chain is governed by a set of state transition probabilities defined by:

$$p_{ij}\,(n, n+1) = \text{Prob}\,[s(n+1) = j \mid s(n) = i],\ j = 0,1 \tag{2}$$

Thus $p_{ij}\,(n, n+1)$ is the conditional probability that the system will be in state j at time (n + 1) given that it is in state i at time n. Our two-state system has four transition probabilities which can be put in matrix form as shown below.

$$p(n, n+1) = \begin{matrix} p_{00}(n, n+1) & p_{01}(n, n+1) \\ \\ p_{10}(n, n+1) & p_{11}(n, n+1) \end{matrix} \tag{3}$$

It should be apparent that each row of P(n, n + 1) adds to unity.

A moment's reflection about the physical nature of the system suggests that the transition probabilities must be functions of time. This is because sunlight intensity is a main contributing factor to oxidant formation and because oxidant buildup times are typically several hours in duration. Thus, for example, the value of $p_{11}(n, n + 1)$, the probability that the system is in state 1 and remains so during the next hour, has to be greater at noon than at sunset. The Houston data clearly exhibit this time dependence, as is shown in Figures 1 and 2. These diagrams contain plots of p_{01} and p_{10}, respectively, for 1974. The 1973 data yield similar plots. It can be seen that the time variation coincides with expectation: the transition from 0 to 1 is most probably around noon and that from 1 to 0 is most probable at sunset. We note that Figure 2 shows no data points for times earlier than 0900. This is because state 1 never occurred prior to 0900 in either 1973 or 1974. However, as shown in Figure 1, at 0800 there is a nonzero probability for the transition 0 → 1. Another feature of interest shown in Figure 2 is that p_{10} shows a generally stable value around 0.37 between 1300-1700. Thus, in this time

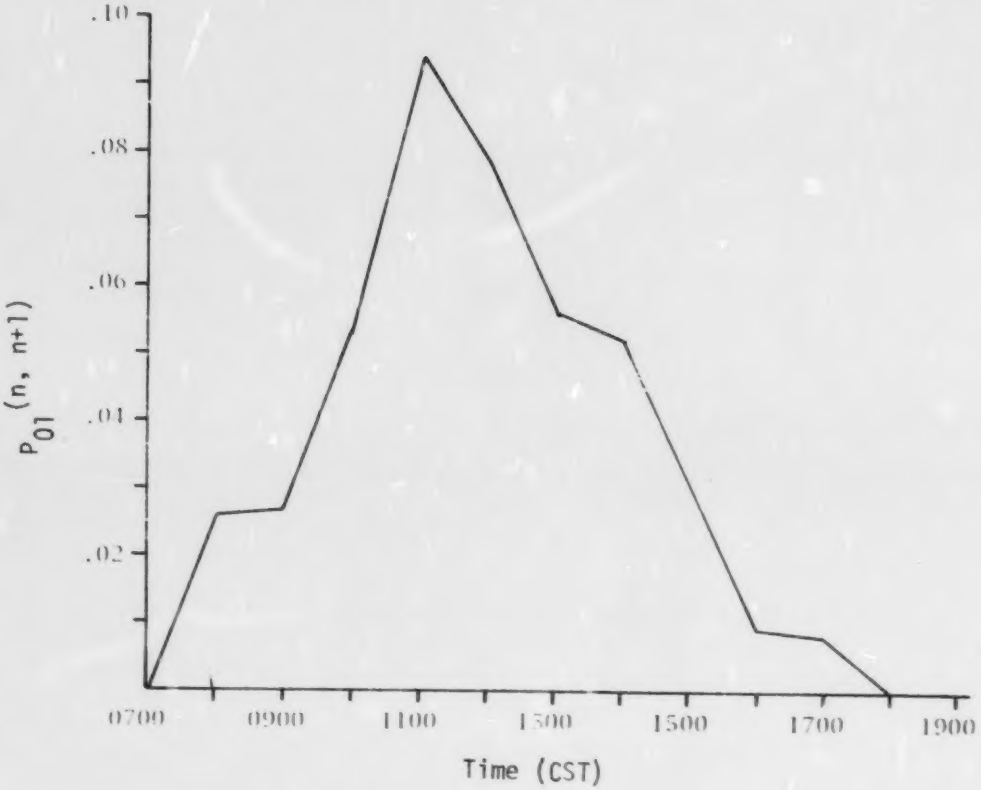

Figure 1. Hourly variation of P_{01}, Houston, May-September 1974.

interval, the probability of remaining in state 1 is high. Finally, we note that after 1900 we are certain of being in state 0. Indeed, between the hours 2000-0800, including the endpoints, state 1 never occurred in the two years of available data examined. The information displayed in Figures 1 and 2 indicates

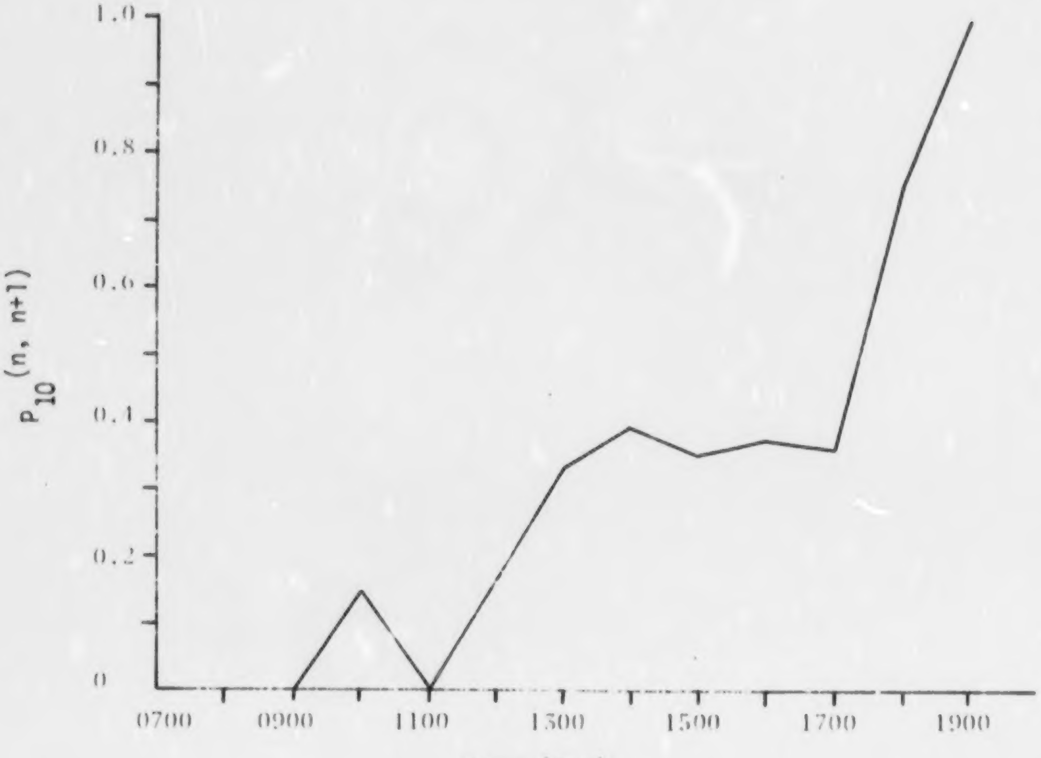

Figure 2. Hourly variation of P_{10}, Houston, May-September 1974.

that we have a diurnal cycle in the transition probabilities with a period of 11 hours.

It is apparent from the discussion that the only parameters required by the model are the state transition probabilities $p_{ij}(n, n + 1)$. One will naturally wonder how these parameters are obtained in order to be able to predict the behavior of the system. This brings us to the important question of causality and the relationship of the p_{ij}'s to such factors as emissions and meteorological conditions. In a later section we discuss a method for finding functions which relate the p_{ij}'s to causal factors.

STRUCTURE OF THE MARKOV CHAIN

The periodicity of the time variations of the transition probabilities is the key factor that leads to a model structure where the transition probabilities appear to be stationary on a diurnal basis. The formulation involves redefining the states of the system and increasing their number. The procedure is as follows. Suppose the cycle has a period of K hours, where K = 11 for Houston. At each one of those hours we have either state 0 or 1 occurring, but the transition probability changes from hour to hour. Let us define

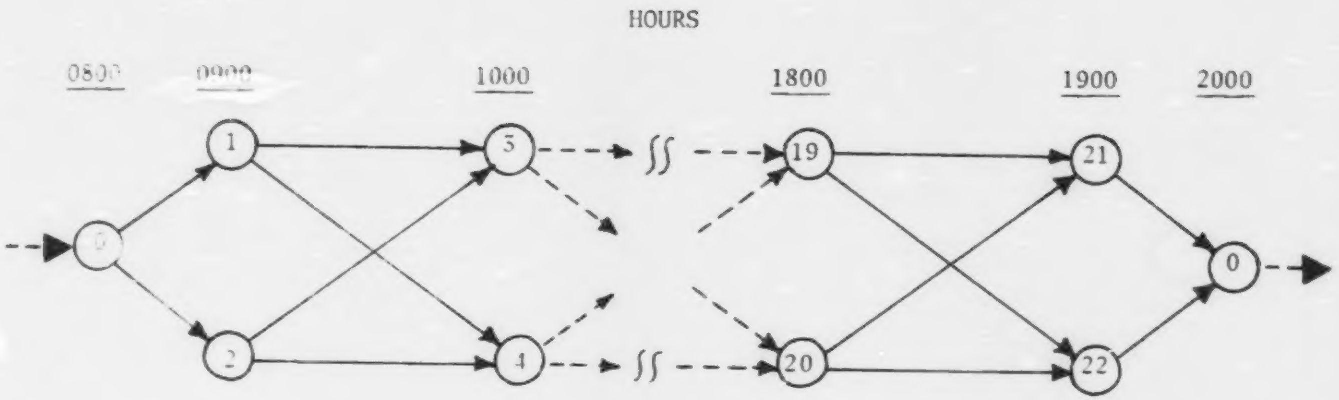

Figure 3. Transition diagram for Houston model.

a new set of 2K distinct states and number them so that the odd-numbered states correspond to state 1 and the even-numbered states to state 0. Thus, at every one of the K hours we have two new states, an even-numbered and an odd-numbered state. For Houston, the expanded chain will have 22 states and is illustrated in Figure 3.

Since the Houston data show that the system is always in state 0 from 2000 to 0800, in Figure 3 the hours from 2000 to 0800 are represented by a single state, also denoted by 0.

To obtain from the expanded chain the probability of occurrence of the original state 1, we simply find the probabilities for the odd-numbered states and add them.

PRELIMINARY TESTING

COMPARISON OF OBSERVED AND COMPUTED STATE PROBABILITY

Preliminary testing was directed at resolving whether or not the model would reproduce the observed limiting state probabilities given a set of transition probabilities calculated from the data. This, of course, does not constitute a model validation test. Rather, it is a test of the algorithm. The results are shown in Table 2 for 1973 and 1974 using data for Houston. Table 2 shows that the limiting state probabilities obtained from the Markov chain are in very close agreement with the observed probabilities. The tentative conclusion that might be drawn from these results is that given a set of physically plausible transition probabilities, we may use the previously described Markov chain to estimate the long-run probability of occurrence of exceedence of the 0.08 ppm threshold oxidant concentration.

TABLE 2. COMPARISON OF OBSERVED AND COMPUTED PROBABILITY OF OCCURRENCE OF STATE 1 FOR HOUSTON, MAY-SEPT. 1973-1974

YEAR	OBSERVED	COMPUTED
1973	.162	.164
1974	.109	.110

ESTIMATION OF TRANSITION PROBABILITIES

For purposes of prediction, it is necessary to obtain a function which relates the transition probabilities of the Markov chain to factors such as emissions and meteorological variables. In this section our discussion will be limited to methodology, since our work on this topic is in progress.

Basically, the problem is one of finding a regression relation for the transition probability as a function of several variables. The logistic function appears to be a convenient model for the desired function. With this model, the transition probability assumes the following form:

$$P_{ij}(t;x_1,x_2\cdots x_N) = \frac{\exp[b_o + \sum_{k=1}^{N} b_k x_k]}{1 + \exp[b_o + \sum_{k=1}^{N} b_k x_k]} \tag{4}$$

where i, j= 0,1, the quantity x_k is the kth independent variable, k = 1, 2, ...N, and N is the number of independent variables. The coefficients b_k are the parameters of the function and are estimated from the data. The method of maximum likelihood can be used to find normal equations which are solved for the parameters b_k (6,7). Sufficient statistics are available for this computation.

We note that in Equation 4 the time dependence is implicit; one would obtain a function such as Equation 4 for each hour of the day instead of obtaining a single such function with time as an independent variable. Also, in Equation 4 the variables x_k would be emissions, temperature, solar radiation, concentrations of other species, wind speed and direction, etc.

Once such a function is obtained, one can manipulate the transition probabilities to determine the effects of changes in emissions. The modified transition probabilities are then spplied to the Markov chain model to obtain the limiting probability of the oxidant concentration exceeding 0.08 ppm during a specified time interval. This limiting probability is then compared with the frequency measure mandated by the NAAQS.

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A PRELIMINARY INVESTIGATION OF THE EFFECTIVENESS OF AIR POLLUTION EMERGENCY PLANS

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ABSTRACT

A study was made of the effectiveness of currently conceived emergency abatement plans for oxidant control. Episodes in the South Coast Air Basin over approximately five years (1970 to September 1974) are characterized by their frequency of occurrence, their duration, and their extent. Using the June 1974 South Coast Air Basin episodes as a test case, and a photochemical air quality simulation model, an objective evaluation of the effectiveness of short-term strategies was conducted. It is concluded that, because of the chemical and meteorological complexities of the episodes, they are extremely difficult both to predict and to control over a short time period.

INTRODUCTION

The air pollution emergency plan provides the basis for taking action to prevent or abate episodes where air pollution concentrations reach levels that could endanger, or cause significant harm to, the public health.

In a recent study, Stanford Research Institute (SRI) undertook a review and assessment of air pollution emergency episode planning in general and the proposed 1975 California Air Pollution Emergency Plan (CAPEP) in particular. The scope of the study was restricted to emergency plans relating to photochemical oxidant concentrations and to the associated proposed short-term control strategies.

The CAPEP relies heavily on prediction, in that abatement action is to be taken if oxidant concentrations are "predicted or reached". The requirement to take action on predictions alone makes CAPEP significantly different from Environmental Protection Agency (EPA) recommendations. Figure 1 presents an example of the action by stages that can be taken to prevent or abate air pollution episodes.

In the technical discussions that follow, historical episodes in the South Coast Air Basin (SCAB) are used in evaluating the control plan. Two particularly relevant, and interrelated, technical aspects are presented:

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STRATEGY	EPISODE STAGE		
VOLUNTARY REDUCTION IN TRAFFIC	STAGE 1 ALERT	STAGE 2 WARNING	STAGE 3 EMERGENCY
BAN GOVERNMENT VEHICLES			
CLOSE ADMISSION TO PUBLIC RECREATION FACILITIES			
CLOSE GOVERNMENT OFFICES*			
BAN FLEET VEHICLES EXCLUDING GASEOUS-FUELED VEHICLES			
CLOSE ADMISSION TO PRIVATE RECREATION FACILITIES			
CLOSE ADMISSION TO REGIONAL SHOPPING CENTERS			
CLOSE SCHOOLS AND COLLEGES*			
CLOSE "DOWNTOWN" RETAIL AND SERVICE BUSINESSES			
BAN DELIVERY SERVICE OF ALL NONPERISHABLES			
IMPLEMENT STATIONARY SOURCE CURTAILMENT PLANS			
BAN NONESSENTIAL SERVICE CALLS			
CLOSE ESTABLISHMENTS WITH 100 OR MORE EMPLOYEES*			
CLOSE ADMISSION TO ALL OTHER RETAIL AND SERVICE ESTABLISHMENTS			
CLOSE INDUSTRIAL SOURCES			

*Additional activities taken when an episode is predicted for next day

FIGURE 1 ARB-SUGGESTED SHORT-TERM OXIDANT CONTROL ACTIONS

1. Characterization of episode stages by their frequency of occurrence, their duration, and their extent, and

2. Objective evaluation of the effectiveness of short-term control strategies in producing significant short-term air quality improvement.

OXIDANT EPISODE CHARACTERISTICS

Before evaluating the control-effectiveness aspects of the plan, it is desirable to understand the characteristics of oxidant episodes, particularly the frequency, duration, and extent of each of the three episode stages: Stage 1 -- alert (0.20 to 0.34 ppm); Stage 2 — warning (0.35 to 0.49 ppm); and Stage 3 — emergency (>0.50 ppm).

Federal regulations imply that an episode condition must be announced and controlled if only a single station reaches one of the three levels. The SCAB is large and has many stations (26 were archived on tape for 1974). Air quality data were obtained from the SCAB for the approximately five-year period 1970 through September 1974.

These data were then used to identify the days and stations that had Stage 1, 2 and/or 3 oxidant values and to tabulate the duration in days of each episode by stages. It must be recognized that a ten-day Stage 1 episode, for example, might include two three-day Stage 2 episodes and one one-day Stage 3 episode. The results of the analysis are shown in Tables 1 and 2, which present the frequency and temporal and geographical extent of these episodes by their stages.

Several major observations can be made from the analysis of the five-year data shown in Tables 1 and 2:

- Only seven Stage 3 episodes occurred in the five-year period.
- Stage 3 oxidant levels did not persist for more than one day.
- No Stage 3 condition existed at more than one station during any emergency episode.
- Of the 50 Stage 2 episodes, 78% lasted two days or less. None lasted more than four days.
- More than 90% of the Stage 2 episodes were limited to two stations or one station.

EFFECTIVENESS OF SHORT-TERM CONTROL STRATEGIES

SCOPE

Notwithstanding the infrequent occurrence of episodes, their limited extent, and the inexact forecast techniques used (Dabberdt et al., 1975), an important question still remains to be answered: Given that there is a reasonable level of confidence that Stage 2 or Stage 3 oxidant levels will be exceeded tomorrow at known locations, what is the probable effectiveness of short-term control strategies (Figure 1)? To seek a resolution to this question, a numerical photochemical simulation model was used, in conjunction with historical aerometric episode data from the SCAB, to predict the oxidant impact of several alternative short-term emission reduction scenarios.

A case-study approach was used to evaluate the effectiveness of various short-term control strategies. The week of 23-28 June 1974 was marked with poor air quality in the SCAB, primarily due to adverse meteorological conditions, weekday emissions, and abundant sunlight. Six stations -- Azusa, Burbank, Pasadena, Pomona, Upland, and Whittier -- reported the poorest air quality conditions. A maximum oxidant value of 44 pphm was measured on 27 June at the Upland station.

The analysis was designed primarily to answer two questions:

1. How effective are the currently conceived short-term emergency strategies for oxidant control likely to be?

TABLE 1. FREQUENCY OF OCCURRENCE OF THREE AIR POLLUTION EMERGENCY STAGES FOR OXIDANT, BY EPISODE DURATION, FOR THE CALIFORNIA SOUTH COAST AIR BASIN

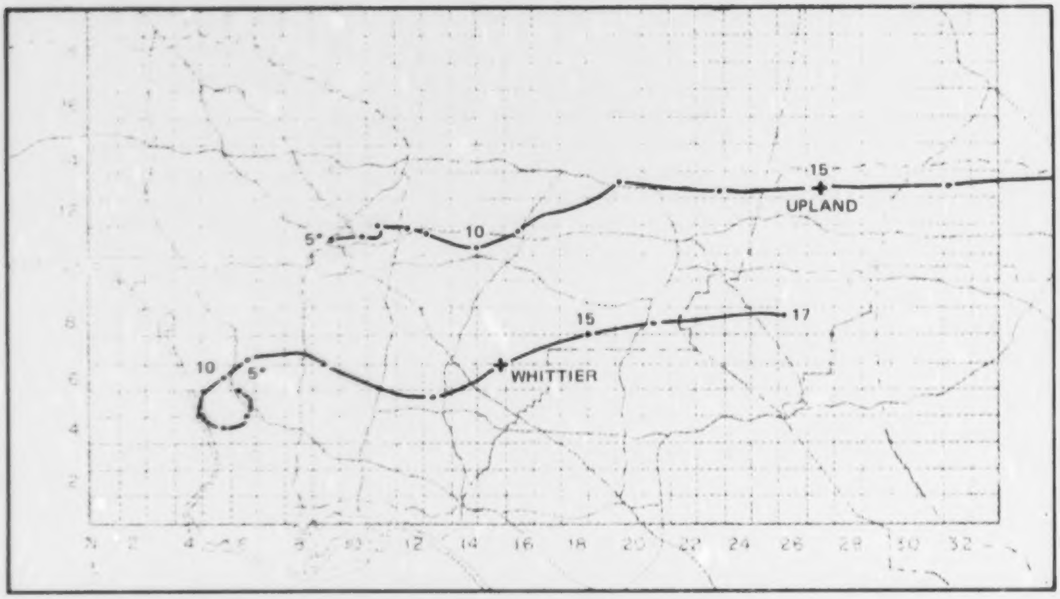
Year	Episode duration (days)	Stage 1: alert (0.20 to 0.34 ppm)	Stage 2: warning (0.35 to 0.49 ppm)	Stage 3: emergency (>0.50 ppm)
1970	1	7	9	3
	2	3	7	0
	3	1	5	0
	4	3	0	0
	5	4	0	0
	6	3	0	0
	10	1	0	0
	67	1	0	0
1971	1	5	3	1
	2	5	0	0
	3	4	1	0
	4	0	1	0
	5	1	0	0
	6	1	0	0
	7	1	0	0
	8	2	0	0
	9	1	0	0
	10	1	0	0
	27	1	0	0
1972	1	14	5	0
	2	5	0	0
	3	5	1	0
	4	3	0	0
	5	2	0	0
	9	1	0	0
	11	2	0	0
1973	1	9	7	2
	2	6	2	0
	3	3	0	0
	4	1	1	0
	5	1	0	0
	6	2	0	0
	7	1	0	0
	11	1	0	0
	14	2	0	0
	14	2	0	0
	18	1	0	0
1974	1	7	2	1
	2	1	4	0
	3	3	1	0
	4	2	1	0
	7	1	0	0
	8	3	0	0
	9	2	0	0
	10	1	0	0
	22	1	0	0

TABLE 2. EXTENT OF STAGE 2 (WARNING) AND STAGE 3 (EMERGENCY) OXIDANT LEVELS, BY EPISODE DURATION, FOR THE CALIFORNIA SOUTH COAST AIR BASIN (MAXIMUM DAILY NUMBER OF MONITORING STATIONS PER EPISODE)

		Frequency of occurrence							
		Stage 2 duration (days)				Stage 3 duration (days)			
Year	Number of stations	1	2	3	4	1	2	3	4
1970	1	7	3	1	0	3	0	0	0
	2	2	4	2	0	0	0	0	0
	3	0	0	2	0	0	0	0	0
1971	1	2	0	1	0	1	0	0	0
	2	1	0	0	0	0	0	0	0
	3	0	0	0	1	0	0	0	0
1972	1	3	0	1	0	0	0	0	0
	2	2	0	0	0	0	0	0	0
	3	0	0	0	0	0	0	0	0
1973	1	7	1	0	0	2	0	0	0
	2	0	1	0	1	0	0	0	0
	3	0	0	0	0	0	0	0	0
1974	1	2	3	0	1	1	0	0	0
	2	0	0	1	0	0	0	0	0
	3	0	1	0	0	0	0	0	0

2. What meteorological and chemical factors influence the effectiveness of such short-term strategies?

Simply stated, the approach entailed: (a) simulating historical atmospheric conditions that existed on selected days by using the DIFKIN (DIFfusion/KINetics) Lagrangian air quality simulation model and (b) projecting the impact of short-term emission reductions on peak oxidant concentrations. The prime motivation in selecting a trajectory model was the ease with which it permits the establishment of a cause-and-effect relationship between emissions and air quality. Operational details of the DIFKIN model have been provided by Martinez et al. (1973) and Ludwig and Kealoha (1974). Two representative trajections were selected for the analysis and evaluation: the first trajectory passed through the Upland station on 27 June at the time (1430 PST) when the peak oxidant level was measured; the second trajectory passed through the Whittier station similarly at 1330 PST on 28 June. The Upland trajectory (see Figure 2) was selected because it was dominated by emissions from mobile sources. The Whittier trajectory, on the other hand, represented a combination of



*This number represents the average time (standard time) between 0400 and 0500 hours and is treated as 0430 hours in the model.

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FIGURE 2 UPLAND (JUNE 27, 1974) AND WHITTIER (JUNE 28, 1974) TRAJECTORIES

emissions from power plants, oil refineries, distributed stationary sources, and mobile sources.

Interpolation between soundings available from the Los Angeles International Airport and El Monte stations was performed by using the model proposed by Edinger (1969) to obtain mixing-height data along the trajectory paths. Eddy diffusivities within the mixing layer, as well as the inversion layer, were calculated according to Hosler (1969).

Considerable effort was made to generate an up-to-date 1974 emissions inventory for the SCAB. After considering the nature of the case trajectories, the 66-x-38-mile grid shown on Figure 2 was selected. The emissions inventory data were divided into five source categories:

1. Freeways [(nitrogen oxides (NO_x), Reactive hydrocarbons (RHC), and carbon monoxide (CO)]
2. Surface streets (NO_x, RHC, CO)
3. Distributed sources (NO_x, RHC)
4. Power plants (NO_x)
5. Oil refineries (NO_x, RHC).

Distributed sources represent emissions from industrial, commercial, and residential sources. Point sources were uniformly distributed over the 2-x-2-mile grid area. A complete description of the emissions inventory was provided by Dabberdt et al. (1975).

Table 3 shows the estimate of pollutant emission reductions under the application of selected control scenarios. Scenarios I and II were designed to correspond to complete and effective implementation of Stage 3 and Stage 2 controls, respectively. Scenarios III and IV, on the other hand, represent exclusive mobile source and stationary source controls, respectively. These emission-reduction estimates were based on analyses and data reported by TRW (1973), the Census of Transportation (1972), the Census of Population (1970) and the Los Angeles Regional Transportation Study (1967); a detailed summary was given by Dabberdt et al. (1975).

TABLE 3. PROJECTED POLLUTANT EMISSION-REDUCTION SCENARIOS

Scenario	Pollutant category	Pollutant Reduction (percent)	Comments
I	Mobile sources	70.5	Appropriate to Stage 3 episode controls
	Distributed stationary sources	25	
	Power plants	50	
	Refineries	35	
II	Mobile sources	47.6	Appropriate to severe Stage 2 controls
	Distributed stationary sources	0	
	Power plants	50	
	Refineries	35	
III	Mobile sources	70.5	Typical of severe vehicle controls alone
	Distributed stationary sources	0	
	Power plants	0	
	Refineries	0	
IV	Mobile sources	0	Typical of comprehensive stationary source controls alone
	Distributed stationary sources	25	
	Power plants	50	
	Refineries	35	

Air quality data were acquired from the Air Resources Board (ARB) for the air monitoring stations operated in the SCAB. Table 4 shows the initial conditions for the two trajectories (0530 PDT). Vertical pollutant profiles were not available. Accordingly, two types of "cases" of vertical profiles were considered. The vertical profiles used in Case 1 are similar to those used by Eschenroeder et al. (1975) for validating the model in the SCAB; they assume maximum initial oxidant concentrations at the surface.

In a recent study, Johnson and Singh (1975) demonstrated the formation and persistence of layers of ozone (O_3) aloft and the implications for the multiple-day, ground-level impact of such layers. Because of the significance of O_3 aloft, Case 2 simulations were conducted for locations where O_3 was assumed to be left over from the previous day. These estimates of elevated O_3 maxima were based on previous-day oxidant levels. Table 4 shows the estimated vertical O_3 profiles for the two cases.

TABLE 4. INITIAL CONCENTRATIONS FOR THE CASES UNDER STUDY
[Whittier Station (W), 28 June 1974; Upland Station (U), 27 June 1974]

Case	Initial conditions	Vertical levels at 0530 hours, standard time (pphm)									
		Level 1		Level 2		Level 3		Level 4		Level 5	
		W	U	W	U	W	U	W	U	W	U
1	NO	7.0	20.0	4.4	12.7	1.0	5.6	1.8	5.0	1.8	4.0
	RHC	42.0	33.0	23.4	18.3	10.4	8.3	8.6	6.8	7.0	4.8
	NO_2	5.0	8.0	4.1	6.5	2.7	4.2	2.2	3.4	1.5	2.3
	O	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	HNO_2	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
2	NO	7.0	20.0	4.4	12.7	1.9	5.6	1.8	5.0	1.8	4.0
	RHC	22.0	25.0	12.1	13.8	5.0	6.3	4.6	5.2	3.3	3.7
	NO_2	5.0	8.0	4.1	6.5	2.7	4.2	2.2	3.4	1.5	2.3
	O_3*	1.0	1.0	12.0	12.0	24.0	24.0	22.0	22.0	20.0	20.0
	HNO_2	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0

*Estimated from previous-day oxidant values.

Note: Level 1: 0-125 m; Level 2: 125-375 m; Level 3: 375-625 m;
Level 4: 625-875 m; Level 5: 875-1125 m.

DISCUSSION OF ASSUMPTIONS

The most pressing problem was to establish unequivocal initial conditions for trajectories originating on land. A lack of adequate network density or a clean sea breeze near the coastal areas can result in a fair amount of uncertainty. Vertical pollutant profiles have traditionally been unavailable, and only recently have attempts been made to obtain comprehensive data bases. Furthermore, there is considerable inaccuracy in assigning a RHC fraction to a relatively clean air mass. Current information from Los Angeles indicates that 58% of total hydrocarbon (THC) (as carbon) is reactive, with an average carbon number of 6.22. Although this is consistent with our choice of initial conditions, no guarantee exists that this fraction does not vary from location to location. An additional problem is associated with emissions from point sources. The accuracy with which trajectories can be drawn from surface wind measurements may not be adequate, and a slight shift in trajectory path can produce some error. Furthermore, elevated sources (power plants) are not adequately treated in any of the present photochemical air quality models, and all emissions are assumed to be at ground level. Despite the many assumptions entailed, it is our experience that the general applicability of such models remains valid and that they are sound tools for decision-making purposes.

RESULTS

To summarize the analytical procedure, the simulation model was first tuned to replicate observed oxidant maxima on two trajectories. Tables 5 and 6 show the agreement between observed and simulated values. Next, the oxidant impact of four emission control scenarios was evaluated for each of two cases of initial pollutant profile conditions. Tables 5 and 6 also summarize the projected effectiveness of the various control scenarios for different trajectories and different initial conditions. From these model simulations, results described below were derived:

- Analysis of the Upland trajectory (dominated by transportation emission sources) demonstrates that, even if the proposed Stage 3 emergency plan could be successfully implemented, a one-day oxidant reduction of no more than 17% would be achieved. The maximum effectiveness of proposed Stage 2 controls would be limited to a 7% oxidant reduction (Table 5).
- Analysis of the Whittier trajectory (characterized by emissions from transportation, distributed, and point sources) indicates that implementation of any of the emergency strategies (Stages 3 or 2) might actually have an adverse or negative effect (i. e., up to a 40% peak oxidant increase) characteristic of South Coast episodes over the short time period (Table 6). A reduction in only mobile sources (Scenario III) would result in a 3% to 5% reduction in oxidant values.
- It is also demonstrated that episodes on a given day will be influenced by the previous day's photochemical events and will similarly affect the events of the following day. Elevated O_3 layers from the previous day will essentially remain intact in upper stagnant layers and will not only disperse downward during the following day, but will also, by reacting with ground-level nitric oxide (NO), be able to significantly affect peak surface O_3 production (Case 3, Table 5).

SUMMARY

From the consideration of episode characteristics, it is clear that Stage 3 (emergency) oxidant levels historically have not persisted for more than a single day at a time; accordingly, the prediction of the onset and termination of a Stage 3 emergency must be timely, accurate, and reliable. Therefore, to be effective, a Stage 3 control strategy must work almost immediately. Stage

TABLE 5. EFFECTIVENESS OF CONTROL STRATEGIES: UPLAND STATION TRAJECTORY FOR 27 JUNE 1974

Case	Historical conditions Measured ozone hourly maxium* (pphm)	 Simulated ozone hourly maximum* (pphm)	Scenario	Simulated ozone maximum* (pphm)	Percent change
1	44	46	I	38	-17%
			II	43	- 7%
2	44	45	I	38	-17%
			II	42	- 6%

*14-1500 PST.

TABLE 6. EFFECTIVENESS OF CONTROL STRATEGIES : WHITTER STATION TRAJECTORY FOR 28 JUNE 1974

Case	Historical conditions Measured ozone hourly maximum* (pphm)	 Simulated ozone hourly maximum* (pphm)	Scenario	Simulated ozone maximum* (pphm)	Percent change
1	33	34	1	43	+28%
			11	47	+40
			111	33	-3
			1V	45	+33
2	33	31	1	37	+17
			11	41	+29
			111	30	-5
			1V	39	+24

3 episodes are not isolated but often occur immediately after Stage 2 episodes. The difference between CAPEP-and EPA-recommended episode plans becomes significant here. According to EPA recommendations, a Stage 3 episode will probably never be called, because one must first measure the occurrence of Stage 3 episode conditions and then predict that these conditions will recur within 24 hours. But Stage 3 episodes have never lasted two or more days. According to CAPEP, however, if conditions show signs of deteriorations at the Stage 2 level, it is possible to institute Stage 3 controls on the prediction that the next day will achieve Stage 3 levels.

It is clear from the above discussion that there is a need for accurate air pollution forecasts of 18- to 24-hour duration. At present, however, no objective techniques with an adequate verification record are available

(Dabberdt et al., 1975). One difficulty is that, although photochemical air pollution is a three-dimensional problem, it is often treated as two dimensional. For example, if a reservoir of O_3 exists entrapped between the upper stagnant layers and is likely to disperse downward, surface measurements of O_3 will not help to predict such a reservoir because of the surface destruction of O_3 by precursors and surface features. Similar limitations apply to surface meteorological information.

A further problem associated with the effectiveness of short-term strategies for oxidant control is the complex kinetics of oxidant formation and the inapplicability of traditional rollback concepts. Case 1, Table 5 clearly shows that even drastic emission controls (Stage 3) can result in only a 17% maximum oxidant relief. Even in the absence of an elevated reservoir of O_3, the impact of reduction in emissions is inherently limited by the high atmospheric pollutant loading and the inherent nonlinearity of the photochemical system. The potential effect of "new" pollutants is therefore limited by the residence time of "old" ones.

The results for the Whittier trajectory are intriguing in that some of the control strategies may actually cause short-term increases in oxidant levels. As is clear from Table 5, a reduction in mobile sources only (Scenario III) would result in a 3% to 5% reduction in oxidant values. Under the application of all the other strategies, the oxidant values for the Whittier station were actually projected to increase by as much as 40% for Stage 2 controls (Case 1). This projected increase is primarily attributable to the fact that the Whittier trajectory passes over at least one power plant and the reduction is net O_3 formation resulting from the institution of emission reduction strategies would be more than compensated by the reduction in O_3 destruction that would probably result from reducing the power-plant NO emissions. It is important, however, to emphasize that the total air pollution potential in a given air mass is always greater in cases where no abatement strategies are applied than in cases where some strategies are applied. The problem is that this potential is not necessarily reduced over a short time period. A look at the RHC-NO_x ratio for the Whittier station showed that, if the trajectory were followed over subsequent days, eventually a net oxidant reduction by the application of these strateiges would probably have been realized. This reduction, however, might occur several days later and many miles downwind. The effectiveness of the short-term strategies must be deemphasized, in that they may provide little or no short-term relief.

So far we have assumed that the strategies could be enforced on a short-term basis under ideal conditions. In actuality, the enforcement problems encountered would be considerable. For example, during a Stage 3 emergency, particularly since a strict enforcement mechanism has not been implemented, it is unrealistic to expect that the population, faced with an unexpected vacation day, would not use automobiles. Socioeconomic factors would likely play an important role, since the cost of a Stage 3 abatement action in the SCAB has been estimated by Dabberdt et al. (1975) to be about $100 million in lost wages alone. Similar Stage 2 actions could result in lost wages up to $45 million. Indeed, such socioeconomic factors may ultimately control the nature and scope of the available short-term control options.

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SESSION 18

OXIDANT-PRECURSOR RELATIONSHIPS AND THEIR INTERPRETATION IN TERMS OF OPTIMUM STRATEGY FOR OXIDANT CONTROL - I

Chairman: J.N. Pitts
University of California

A "J" RELATIONSHIP FOR TEXAS

H. M. Walker*

ABSTRACT

An upper limit curve relationship has been contracted for more than 900 ozone-non-methane hydrocarbon data pairs obtained by the Texas Air Control Board monitoring network since 1973. Unlike the AP-84 curve, the Texas Air Control Board curve interests the .0 6-9 a.m. non-methane hydrocarbon axis at .125 ppm ozone. It also reaches a maximum at 1.1 ppm 6-9 a.m. non-methane hydrocarbon, and then descends to values below the National Ambient Air Standard for ozone at levels above 5.0 ppm non-methane hydrocarbon. Fifty-nine data pairs from the Houston Air Pollution Control District network move the maximum out to 2.4 ppm, but do not change the shape of the curve. The possible implications of the Texas "J" curve are discussed.

INTRODUCTION

The concept of the upper limit curve as a device for developing a meaningful empirical relationship between atmospheric oxidants and atmospheric hydrocarbons (HC) was first annunciated by Schuck and Altshuller et al. in an article in the Journal of the Air Pollution Control Association published in May, 1970 (1). While these authors gave several graphs, the one (Figure 1) relating maximum daily one-hour average oxidant in ppm to 6-9 a.m. average non-methane hydrocarbons (NMHC) concentrations in ppm carbon was probably the most significant. Shortly thereafter, this graph, with some change in the positioning of the line, was published as Figure 4-2 in AP-84, the Criteria Document for Nitrogen Oxides (2) (Figure 2). On August 14, 1971, the Environmental Protection Agency (EPA) finalized its requirements for State Implementation Plans. This document contained Appendix J -- a curve relating the degree of HC reduction required to attain the 0.08 ppm oxidant standard to the current ambient oxidant level. Appendix J was derived from Figure 4-2 of AP-84 (Figure 2). Thus, the upper limit curve correlation became the technical basis of the legally-required strategy for HC control in the United States.

A brief review of the conceptual basis of the upper limit curve analysis seems appropriate. Technically, a dependent variable (oxidant level) might be a function of ten independent variables (perhaps HC concentrations, nitrogen oxides (NO_x) concentration, temperature, incident sunlight, HC composition, humidity, mixing height, initial ozone (O_3), free radical initiators, etc.).

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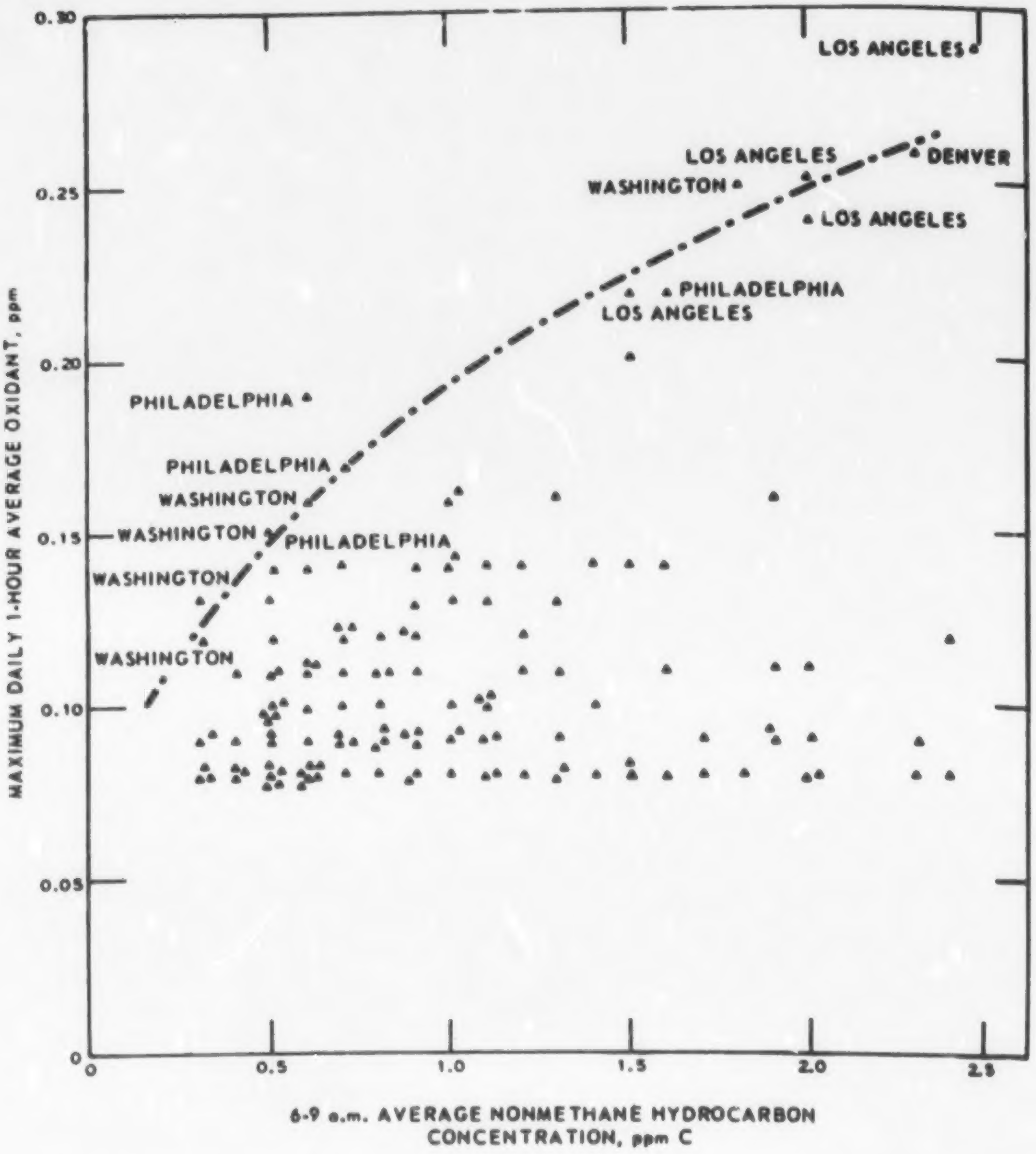

Figure 1. Maximum daily oxidant as a function of early morning non-methane hydrocarbons, 1966-1968 for CAMP Stations; May through October 1967 for Los Angeles.

The upper limit concept assumes that, if enough data is available covering a wide range of all variables, some points will be found where the combined effect of all variables except the one under study will be most favorable for a maximum level of the dependent variable. Thus, if one plots enough data relating maximum daily oxidant to 6-9 a.m. NMHC, the plotted upper limits

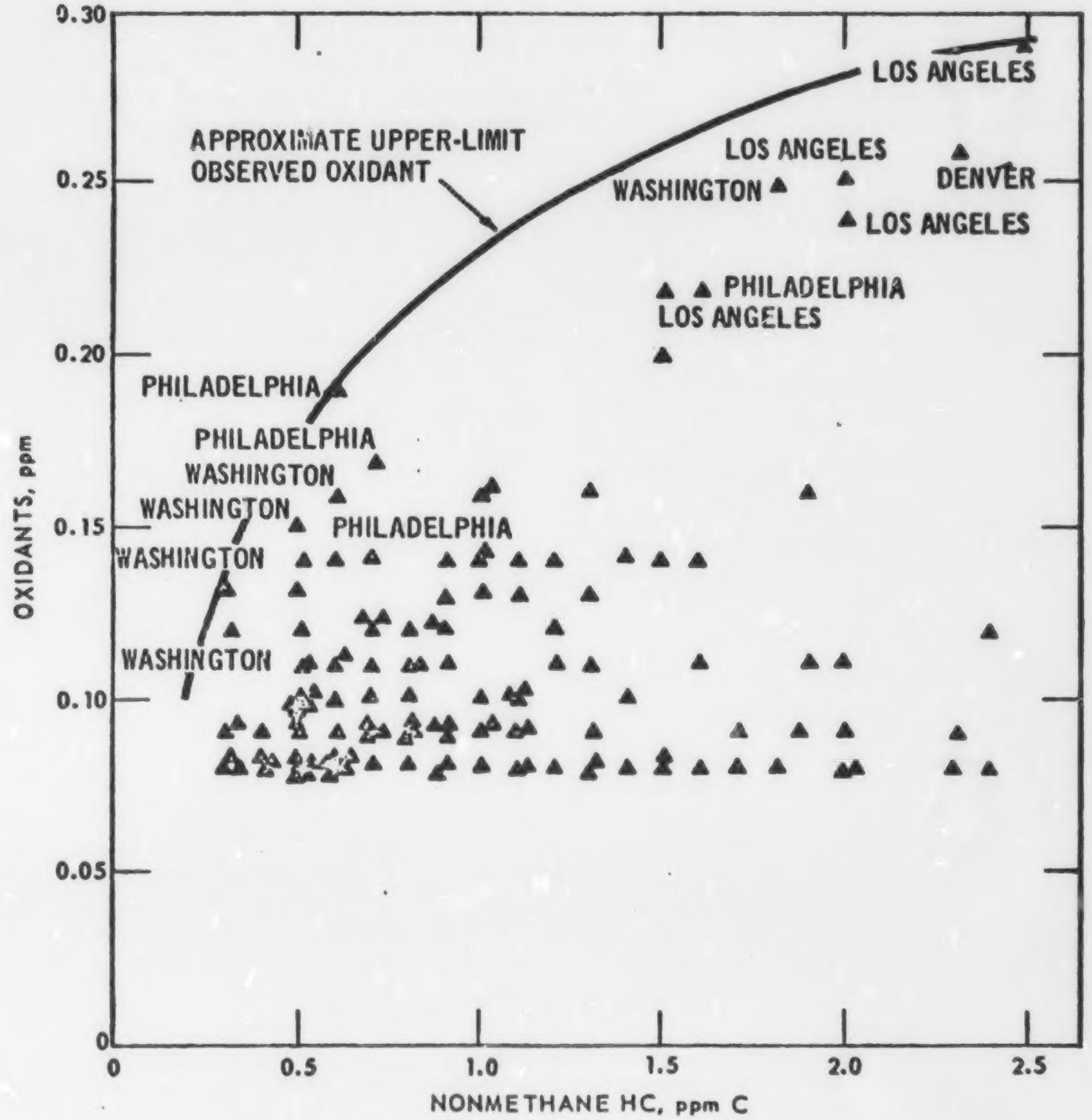

Figure 2. Maximum daily 1-hour-average oxidants as a function of 6-to-9-a.m. averages of nonmethane hydrocarbons at CAMP stations, June through September, 1966 through 1968, Los Angeles, May through October 1967. (Figure 4-2 of AP-84.)

of the observed values are deemed to represent the maximum oxidant level possible at the corresponding HC concentrations. Such a relationship can become the basis of a strategy for controlling the dependent variable on the basis of the chosen single independent variable -- as indeed it has. Probably no piece of technical analysis has ever become more controversial.

While the basic concept is logical and acceptable, the practical problems with the approach are enormous. Among the more significant weaknesses are:

- The approach is totally dependent upon the most extreme values of either variable -- thus the final result tends to depend primarily upon those values most suspect by conventional methods of data correlation and data validation.

- Because of the reaction time required for oxidant formation and wind effects, the two variables are not measured for the same air sample. Typically, the observations are removed in time by 3-8 hours and in distance by 10 to 100 miles.

- There is no way to judge whether or not sufficient data is at hand to yield an adequate upper limit curve. Ultimately this becomes a matter of statistical analysis. Perhaps a useful control relationship might be derived from a set of maxima that occurs once in 25 observations, whereas a relationship based upon levels that occur but once in 500 observations might represent a meaningless study of rare phenomena.

- The dependent variable chosen may not actually be functionally related to the independent variable being analyzed.

Laboratory data has, in general, qualitatively supported the HC/oxidant relationship of the Schuck and AP-84 upper limit curves. Aerometric data have, in general, failed to confirm the relationship and have yielded many conflicting results with uncertain conclusions. As a result, Appendix J has fallen into disrepute and is no longer supported by any major group. The replacement rollback relationship does not have an experimental basis of support and seems to be used merely as a legal tool, attractive because of its great simplicity.

THE TACB UPPER LIMIT CURVE

Early in 1975 a staff member of the Texas Air Control Board (TACB), G. K. Tannehill, constructed an upper limit curve based on limited 1973-74 TACB "Connie" monitoring network data (3). This curve had a greatly different shape than the original upper limit curves and it had different implications (Figure 3).

This work was never published, but it was cited to an EPA technical panel in a public discussion held in St. Louis last January, and it provoked strong disagreement. One of the objections was that it was not based upon a sufficiently large data sample. Since much more data is now available from the Texas network, and because of its wide geographical coverage and the extremely high standards employed by the Texas monitoring network, a repeat of

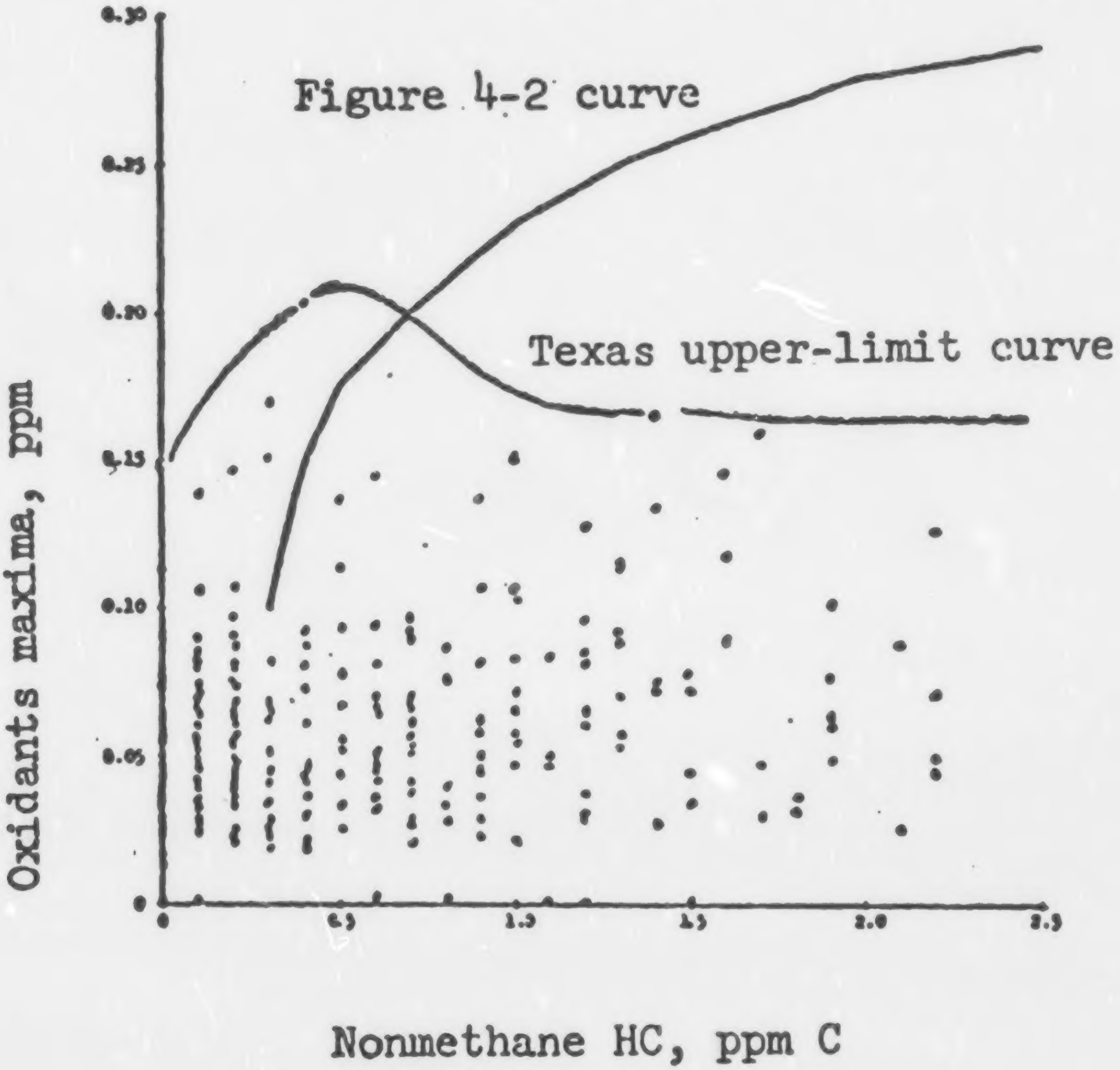

Figure 3. The TACB upper-limit curve compared to the Figure 4-2 curve of AP-84.

the study based upon the latest information was deemed justified. This paper reports the results of that study.

For simplicity and clarity, the plotting was done year-by-year and the results were finally combined by tracing. Figure 4 presents data for the two-year period 1973-1974. There simply was not enough valid data from 1973 to attempt an independent analysis.

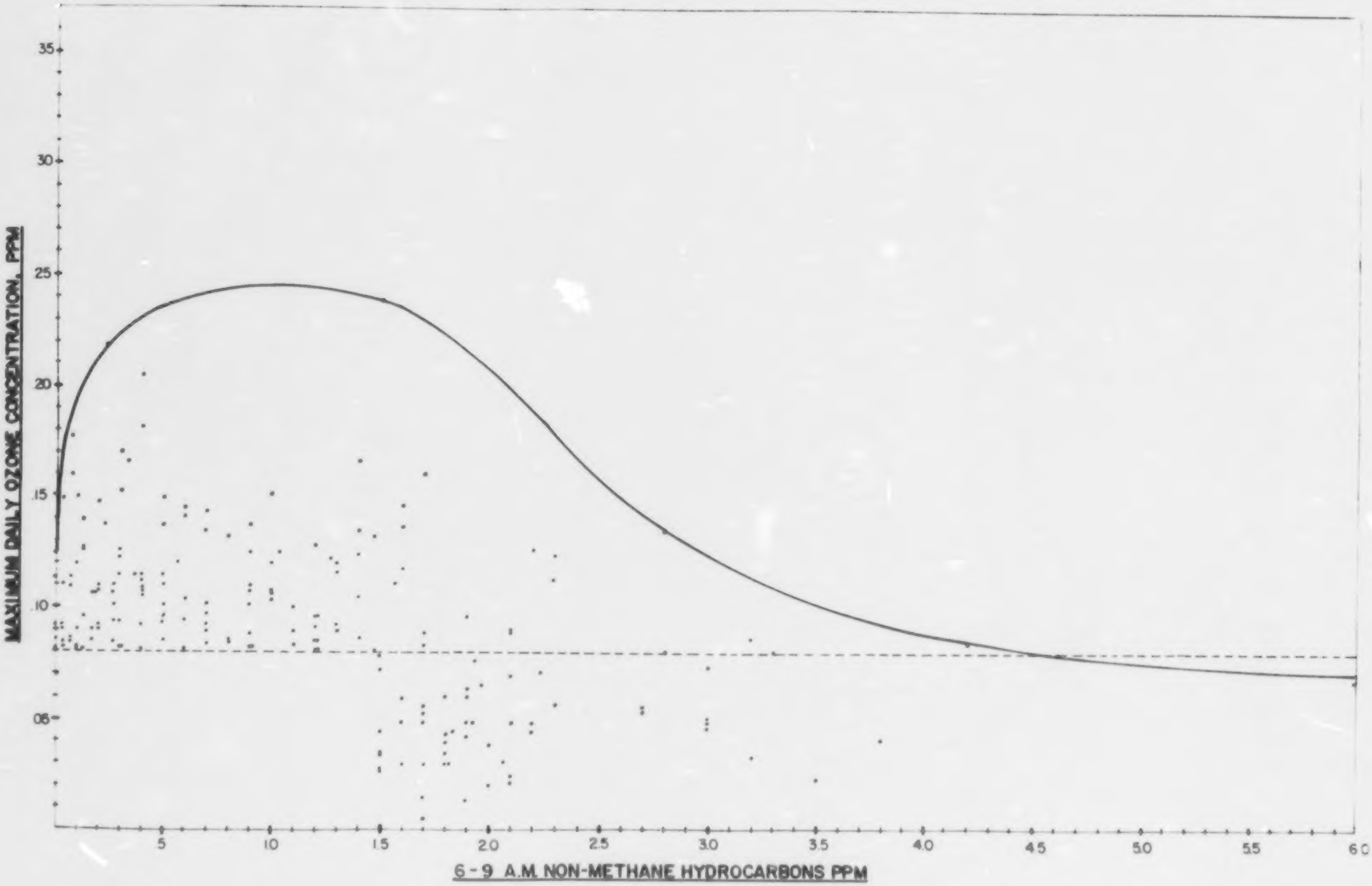

Figure 4. Ozone vs. 6-9 a.m. hydrocarbons; two years (1973-1974)
TACB Connie network.

The procedure followed was straightforward. Copies of computer pages giving hour-by-hour values for both ozone and NMHC were furnished by the TACB. Computer-derived 6-9 a.m. NMHC averages were also provided. The oxidant values were eye-scanned for daily maxima. These data were first tabulated and then plotted. All days were plotted that had valid values for 6-9 a.m. NMHC and maximum oxidant and reached 0.08 ppm ozone or more, or equalled or exceeded 1.5 ppm 6-9 a.m. NMHC. In these respects all of these plots are completely comprehensive. All of the points meeting these criteria appear on the appropriate graphs.

Initially it had been planned to also include all points when the daily mean NMHC equalled or exceeded 1.0 ppm. However, this proved excessively laborious; therefore, this criteria was abandoned rather early in the study. Some points from this group, however, were plotted, which in many cases led to points where ozone peaked below 0.08 ppm and the 6-9 a.m. NMHC was also below 1.5 ppm. This accounts for the scattered points in the lower left-hand corner of the 1975 graph. These were not deleted even though they in no way affect the upper limit curve, because they serve as a reminder that the lower left-hand block really contains thousands of points, should one have the perseverance to plot them.

Commenting specifically on the 1973-74 plot, it essentially used the same data as Tannehill's earlier analysis with essentially the same upper limit curve resulting.

Plotting the 1975 data yielded a similar result (Figure 5). At this point let me discuss a detail that may provoke later questions. TACB reports NMHC values only to one-tenth percent on the basis that the accuracy of the analytical method does not justify reporting hundredths of a percent. Discussion with TACB staffers revealed that all of their computer data processing involves the use of truncation rather than rounding. Thus, the instrumental data is first averaged for the hour and then truncated to the significant tenth ppm. In creating the 6-9 a.m. NMHC average, these truncated values are averaged and again truncated to the significant tenth. This system, on the average, will understate the latter value by 0.1 ppm but under some circumstances can understate by as much as .167 ppm. Some values are not understated at all by the system. TACB is now modifying these programs.

While this procedure provides strong legal protection against any risk of overstating pollutant data values, it is not desirable for a scientific analysis. When this feature was discovered, the first three years of data had already been plotted. A total repeat with hand-averaging was simply not possible. However, high accuracy in the hydrocarbons (HC) values is only critical at the lowest levels. Therefore, new averages were calculated by hand for all 6-9 a.m. NMHC values originally reported as .0, .1 and .2 ppm. No attempt was made to round back to the nearest tenth ppm, but the data were simply replotted at the averaged value to the nearest one-hundredth ppm. Thus, we have points at .03, .07, 13, .17, .23 and .27 on the left-hand section of the graphs, but mostly only at integral tenths of ppm in the remainder. In general, about 1/3 of the points so processed increased by .03; 1/3 increased by .07; and 1/3 did not increase. Therefore, on the average, the bias in the data removed by this effort was .03 ppm. There was no way to compensate

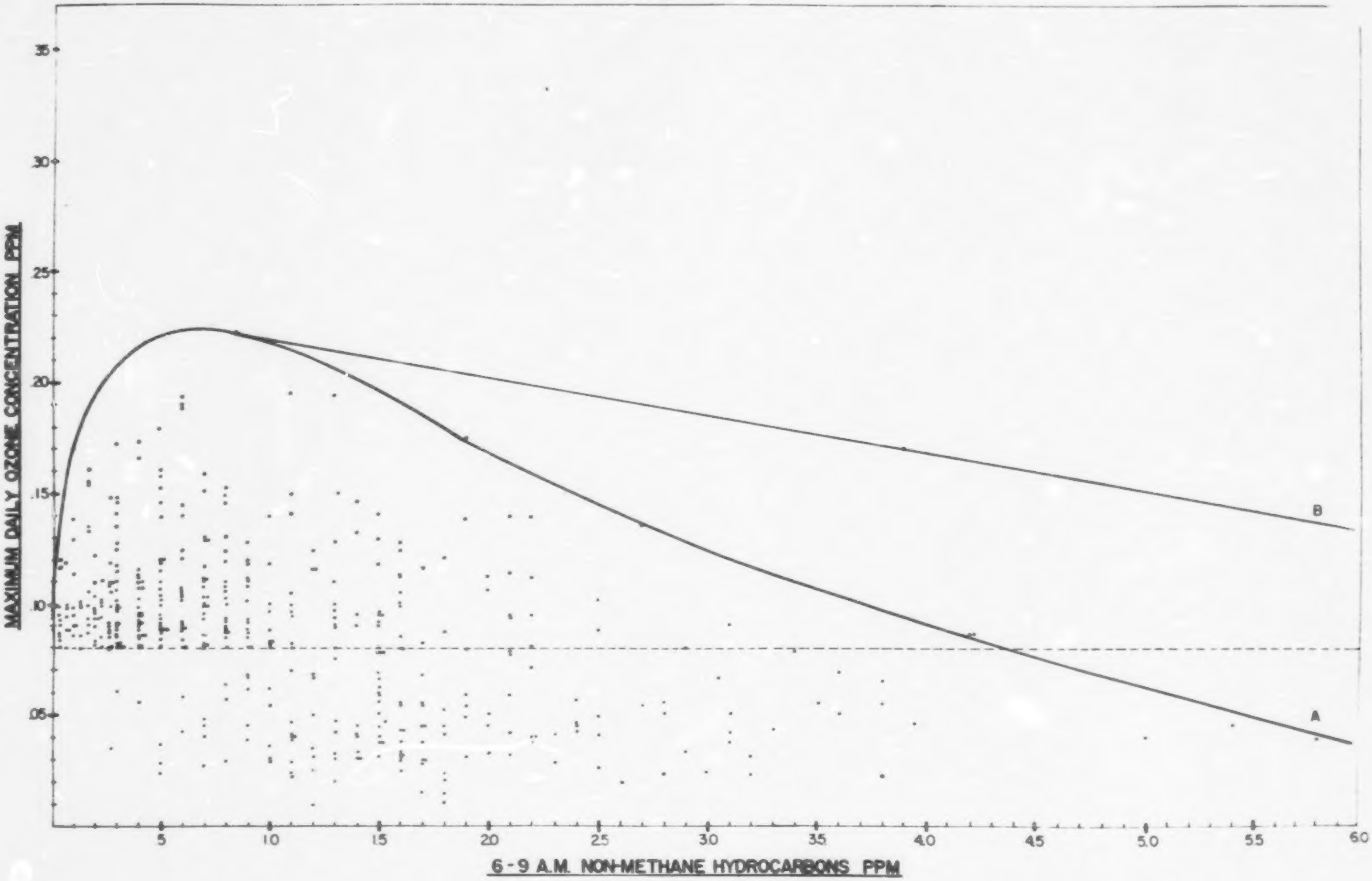

Figure 5. Ozone vs. 6-9 a.m. hydrocarbons; full year 1975 TACB Connie network.

for the original truncation error, which should amount to 0.05 ppm on the average. Therefore, it is believed that all values of less than 0.3 ppm are on the average understated by 0.05 ppm and most of the remainder of the values are understated by 0.08 ppm. This has nothing to do with any possible instrumental or sampling errors.

Commenting on the upper limit curve for 1975, there was uncertainty about one point that appears wild. For the moment two choices, A and B, are shown for the curve.

The curve for the first six months of 1976 (Figure 6) differs little from those of the previous three years. It is a striking testimony to the increased scope and efficiency of the TACB monitoring system that the first half of 1976 yielded 310 valid, plottable data pairs, whereas the entire year, 1973, yielded only 30 such pairs. Of course, there are now many more stations than in 1973; but of equal importance is the increased on-stream factor for the HC analyzers.

THE COMPREHENSIVE TACB UPPER LIMIT CURVE

Figures 4 through 6 have traced the development of the data year by year. Figure 7 gives the final result -- the comprehensive Texas upper limit curve based on all valid data available from all fourteen Connie monitoring stations of the TACB network. This is almost the final result of this study.

In drawing the final curve, the single Houston data point at .170 ppm O_3, 3.9 ppm HC was ignored as an outlier. This was largely done on the basis that to use this point would have resulted in a curve inconsistent with the curves for the other years.

What can we say about this curve? First it differs from the original curves in two major respects. The left end of the curve intersects the Y axis at .125 ppm O_3, suggesting that there is no way to reduce ozone maxima below that level by HC control alone. This high intercept is established because this analysis did not exclude HC points below 0.3 ppm as did the original. There are 123 validated pairs of values in this range. This cloud of points effectively blocks any approach to the origin after the manner of the AP-84 curve.

There are ten days when all three hours contributing to the 6-9 a.m. average were reported as .0; 16 days when two of the three hours were .0 and the other hour was .1, and 13 days with a .0, .1, .1 or similar pattern. As was pointed out earlier, the computer system used does not guarantee that any of the values were really .0. Statistically, several would have been expected to be .0 and the average for these 39 lowest points would be expected to be .05 ppm. It would not, however, be reasonable to attempt to drop the curve to the origin down a slot only 0.05 ppm wide. As a practical matter, it would have been more justifiable to flatten the curve and intersect the axis at 0.16 ppm.

The technical implication of this is, of course, that background ozone or ozone not generated because of local HC concentrations can amount to as

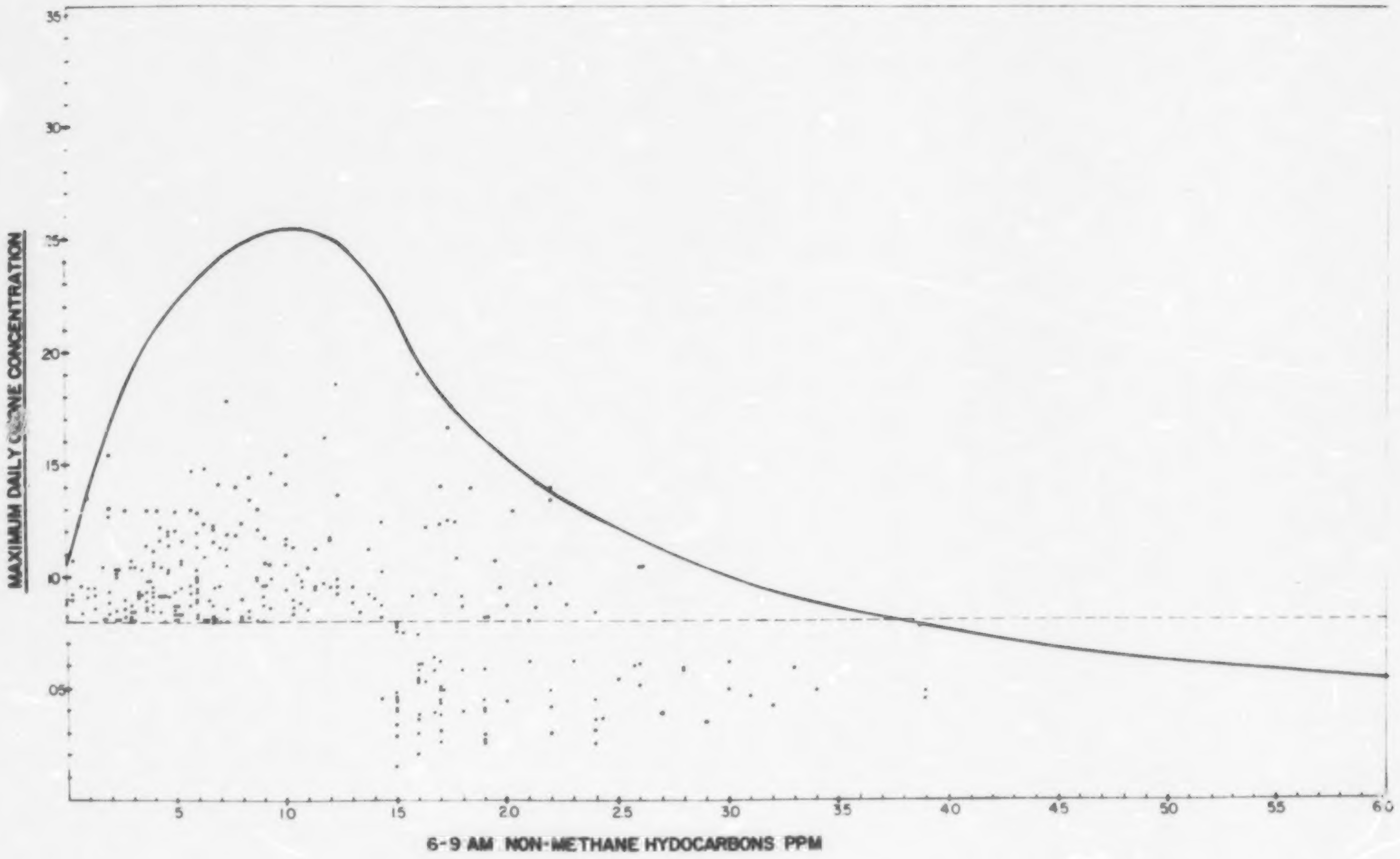

Figure 6. Ozone vs. 6-9 a.m. hydrocarbons; 1st half-year 1976, TACB Connie network.

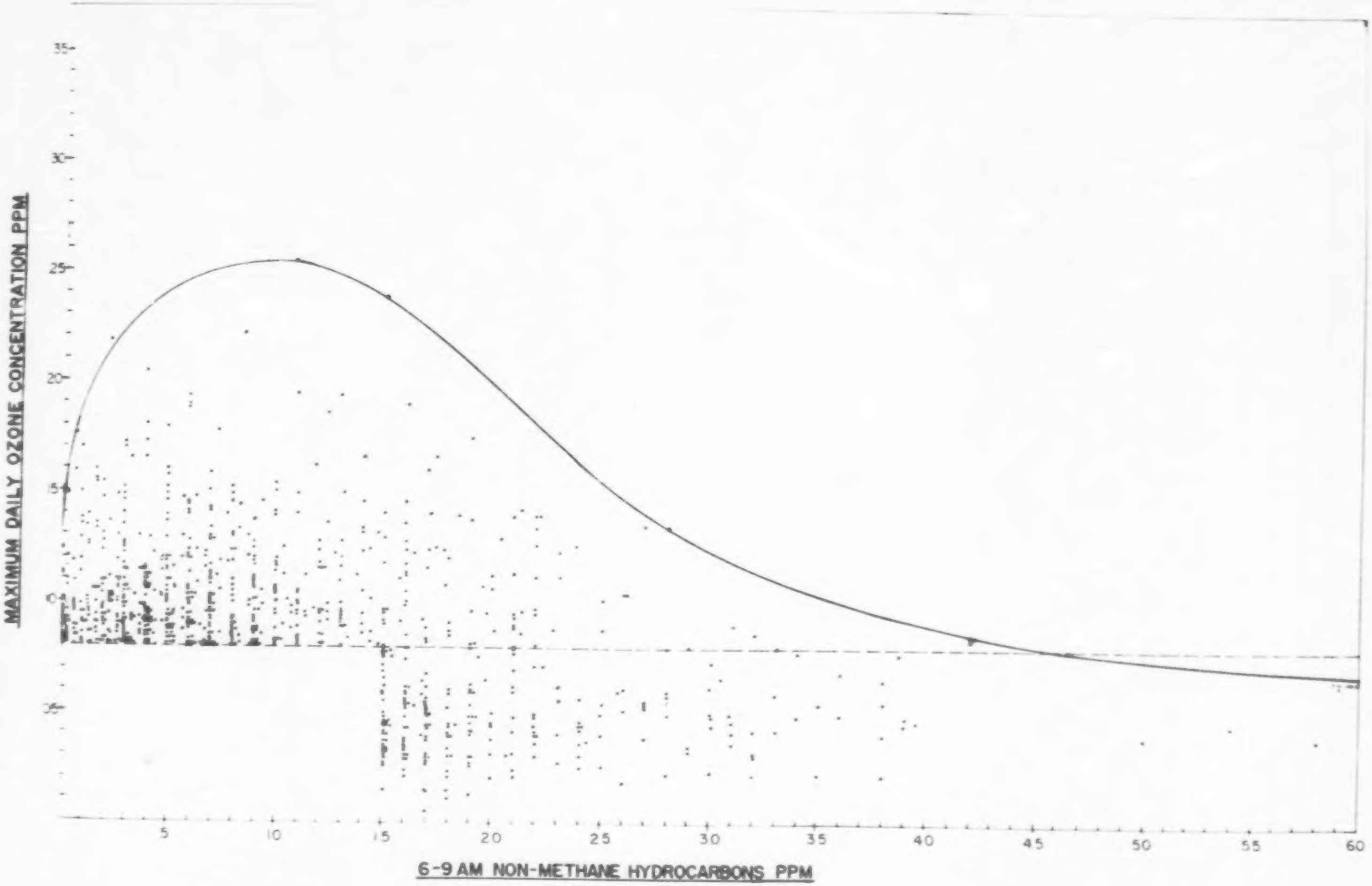

Figure 7. Ozone vs. 6-9 a.m. hydrocarbons; 3 1/2 years, 1973 thru 6/76, TACB Connie network.

much as .125 or even .16 ppm. This is certainly consistent with many of the recent reports of rural ozone, mountain-top ozone, aerial ozone, etc. where high values are found with no concomitant HC found in the ranges detectable by a Beckman 6800-type NMHC analyzer.

While EPA has recently cast doubts upon the value of all data from the Beckman 6800-type instrument, it is still the best instrument available for long-term monitoring of NMHC, and it has provided the national data base to date, including that used in the original Schuck and Altshuller study as well as in this study. Many improvements have been made in instrument operation in recent years and both of the Texas monitoring groups report that, although it is a subtraction-type instrument, negative NMHC values are seldom obtained. This fact and the basic scheme of the instrument suggests that if there is any instrumental error, there is a greater likelihood that high values will be produced rather than low values. This fact was also confirmed by the Scott study of NMHC analyzers (4).

All factors considered, it is probable that the intersection of the upper limit curve with the Y axis at a level well above the national ambient air standard (NAAS) of 0.08 ppm is a valid result and will have to be reckoned with.

The other and more surprising feature of the Texas upper limit curve is that it reaches a maxima at 1.1 ppm and then descends to values below the NAAS at HC levels above about 5 ppm.

The chemical explanation of this may be that above 1.1 ppm the rate of ozone destruction reactions increases more rapidly with HC concentration than does the rate of ozone formation.

This reverse slope also suggests that in areas of excessive HC concentration, reduction will increase ozone maxima until levels below the 1.1 ppm peak are reached. Abatement beyond this point would, of course, result in a reduction. This may have been the reason for the observed increases in ozone maxima observed in several Texas cities after the institution of HC control measures, as reported by Tannehill (5).

Some may argue that the Texas curve drops at HC levels above 1.1 ppm simply because sufficient points do not exist at the higher levels to assure that the maximum combination of all other variables has been attained. This is a valid question. In fact, Altshuller noted the tendency for the plot to deteriorate into a scatter diagram as the number of data points is decreased.

However, one should note that this study involves about seven times as much data as the Altshuller study. There are 263 points at levels of 6-9 a.m. NMHC above the maxima of the curve. Since not one of this large number of points indicates a further rising relationship, the analysis seems rather conclusive in pointing to the validity of the up and over shape for the curve.

It is regrettable that 6-9 a.m. NMHC values were not available for more days with ozone levels above 0.20. In the entire 3 1/2 years, only five valid pairs were recorded when ozone was above that level. At the same time, 11 additional instances of such ozone levels were recorded without simultaneous HC measurement. Of these, four were above 0.25 and two were above 0.3. The highest of all, 0.38, was recorded in Nederland in March, 1973.

THE HOUSTON AIR POLLUTION CONTROL DISTRICT DATA

In an effort to find other data, the Houston Air Pollution Control District (HAPCO) was contacted. A data set containing 59 pairs, all from three city sites during 1975, was furnished. This information had been reported by McKenzie et al., (9) at the Dallas oxidant symposium. When these were plotted, they were found to be quite different from the previously reported data. Two pair above 0.25 ppm ozone (one 0.29 ppm) were in the set which, of course, raised the curve maxima somewhat. The HAPCD HC concentrations were, in general, several ppm higher than the TACB points. Figure 8 shows the effect of adding these points to the previously-developed curve. Essentially the shape remains unchanged, but the maxima is higher and has moved out to 2.4 ppm 6-9 a.m. NMHC.

What is the reason for the apparent inconsistency of the two data sets? To answer this a comparison was made of data that was on hand from the two networks. Specifically, TACB's Mae Drive Station was compared with Houston's Clinton Drive site. The two are both industrially oriented and are only about one mile apart; the Houston city site is slightly over one mile from an industrial area; TACB's Mae Drive site is about twice this distance. The observed ratio of monitored NMHC's was 1.45, Clinton over Mae. The TACB Aldine and HAPCD Parkhurst sites are both on the north side of Houston about six miles apart. Both are suburban; Parkhurst is at least five miles from the ship channel industrial area; Aldine is eleven miles in the same direction. The monitored NMHC ratio was Parkhurst over Aldine 3.29 to 1. This was for 20 days during the late summer of 1975 when both sites monitored HC. The Mae Drive - Clinton Drive comparison was for 16 days.

It is thus clear that the HAPCD sites on the average ran more than twice the NMHC level of the TACB sites. Since such mesoscale discontinuities in HC values would not be expected to be matched by a mesoscale change in ozone maxima, it becomes clear why the HAPCD points gave a curve with a maxima more than twice that of the TACB curve.

It has been suggested that the upper limit concept may be city-specific. This analysis suggests that it is probably site-specific. The more important result is that the HAPCD upper limit curve has the same overall shape as the TACB curve.

One further analysis was attempted. All of the ozone data was plotted versus daily mean NMHC and an upper limit curve was constructed (Figure 9). This curve is essentially the same as the prior curve, except for a considerably shortened HC axis. The outlier point moved back into the pack, offering some justification for the previous decision to ignore this point. The utility of the maximum ozone versus daily mean HC plot appears equal to that of maximum ozone versus 6-9 a.m. HC curve.

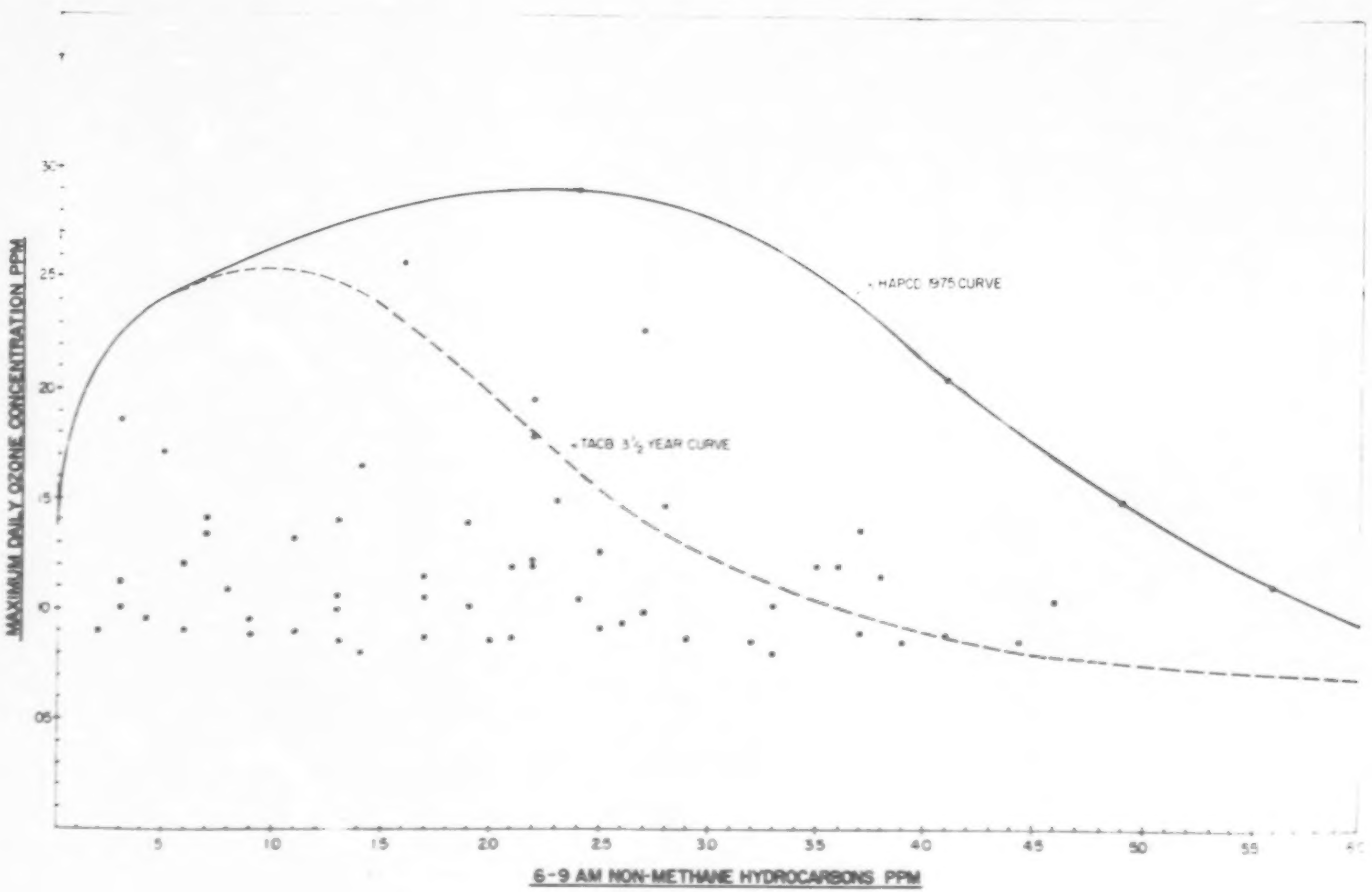

Figure 8. Ozone vs. 6-9 a.m. hydrocarbons; full year 1975, Houston Air Pollution Control Department.

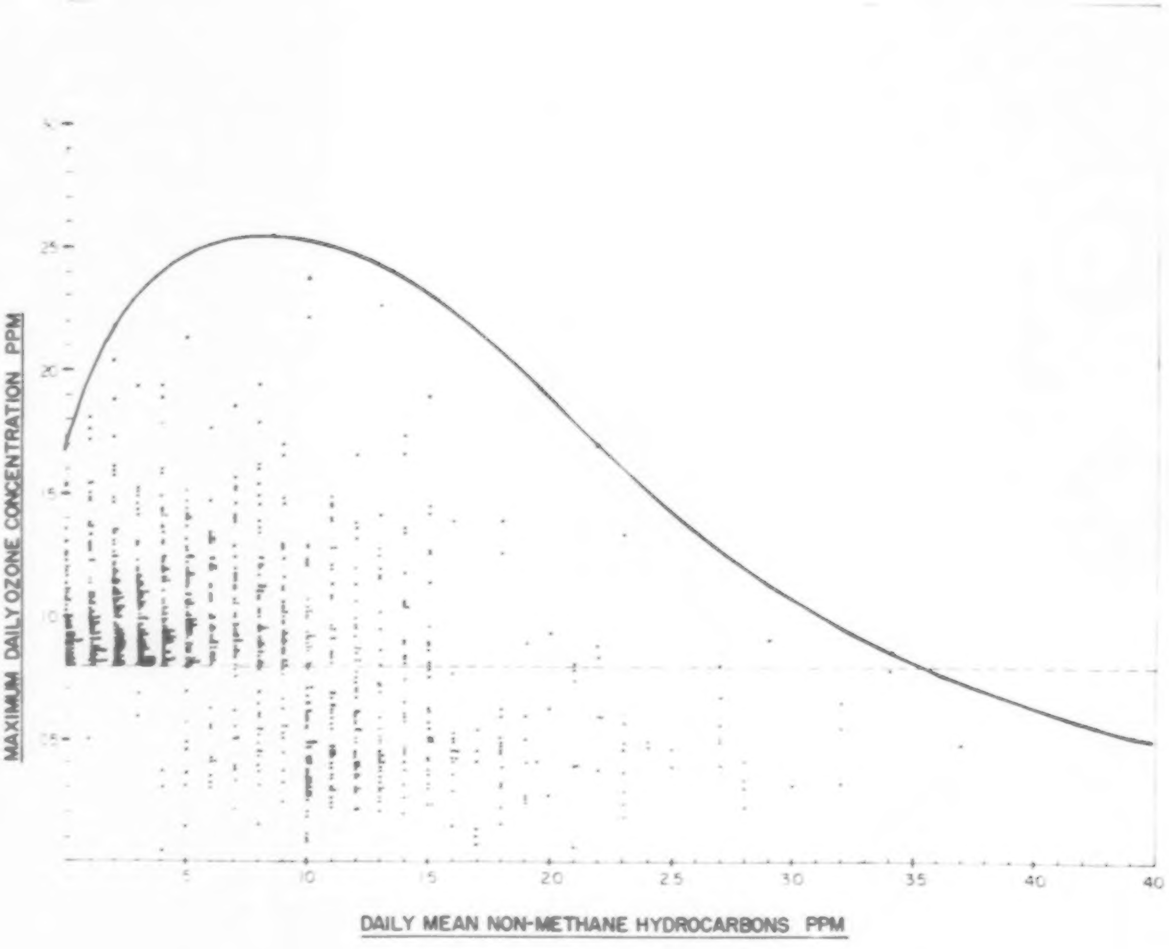

Figure 9. Ozone vs. daily mean hydrocarbons; 3 1/2 years, 9/73 thru 6/76, Texas Connie network.

All of the results argue strongly that there is a major maxima in the ozone HC functional relationship. Is this consistent with laboratory work and theoretical analyses? To examine this point it is noted that several analyses have been made of the ozone-HC-NO_x relationship. An early one was that of Dimitriades (6) whose 1972 graph in Environmental Science and Technology indicated a slope to the isopleth line for 0.1 ppm oxidant that implied increased oxidant with reduce HC in the region of low NO_x (Figure 10). This was more fully developed by Hecht and Seinfeld (7), who were able to plot a family of ozone isopleths versus NO_x and HC (Figure 11).

On Figure 12, a similar plot by Quon and Wadden (8) is reproduced. The shaded area is the area where 90% of all TACB monitoring points fall. All of the Texas sites must be characterized as having very high HC-to-NO_x ratios. These vary widely, but typically range 17.5/1 to 70/1 for the cities in Texas having the higher HC levels. Referring to Figure 12, in the region of the Texas data where HC are above 1.0 ppm, a simple reduction in these levels will increase, not decrease, ozone. Only after the axis of the isopleths are passed at about 1.0 ppm will HC reduction produce oxidant reduction. At the St. Louis discussions, it was stated that a maxima would be found only above a 12.5/1 ratio of HC-to-NO_x. The Texas ratios appear to be generally well above that level. Thus, the shape of the Texas upper limit curve is consistent with these theoretical considerations.

SUMMARY

1. The Texas upper limit curve intersects the .0 hydrocarbon axis at an ozone level well above the ambient air standard, reflecting background ozone of various types. This is in agreement with recent field studies.
2. The Texas curve has a pronounced maxima. This would be expected from theoretical considerations.
3. The upper limit analysis appears to be site-specific.
4. Plotting maximum ozone versus daily mean HC yields results similar to plotting versus 6-9 a.m. HC, except for the shortened axis.

ACKNOWLEDGEMENTS

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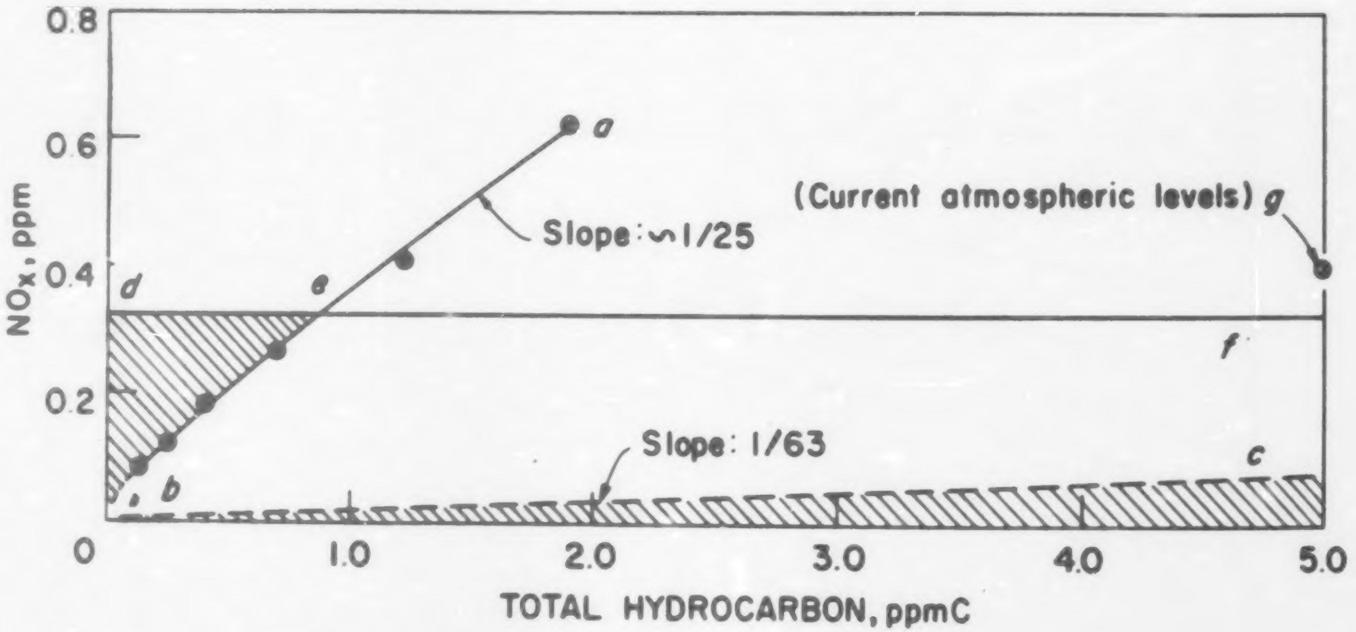

Figure 10. Oxidant isopleth line for 0.1 ppm oxidant.

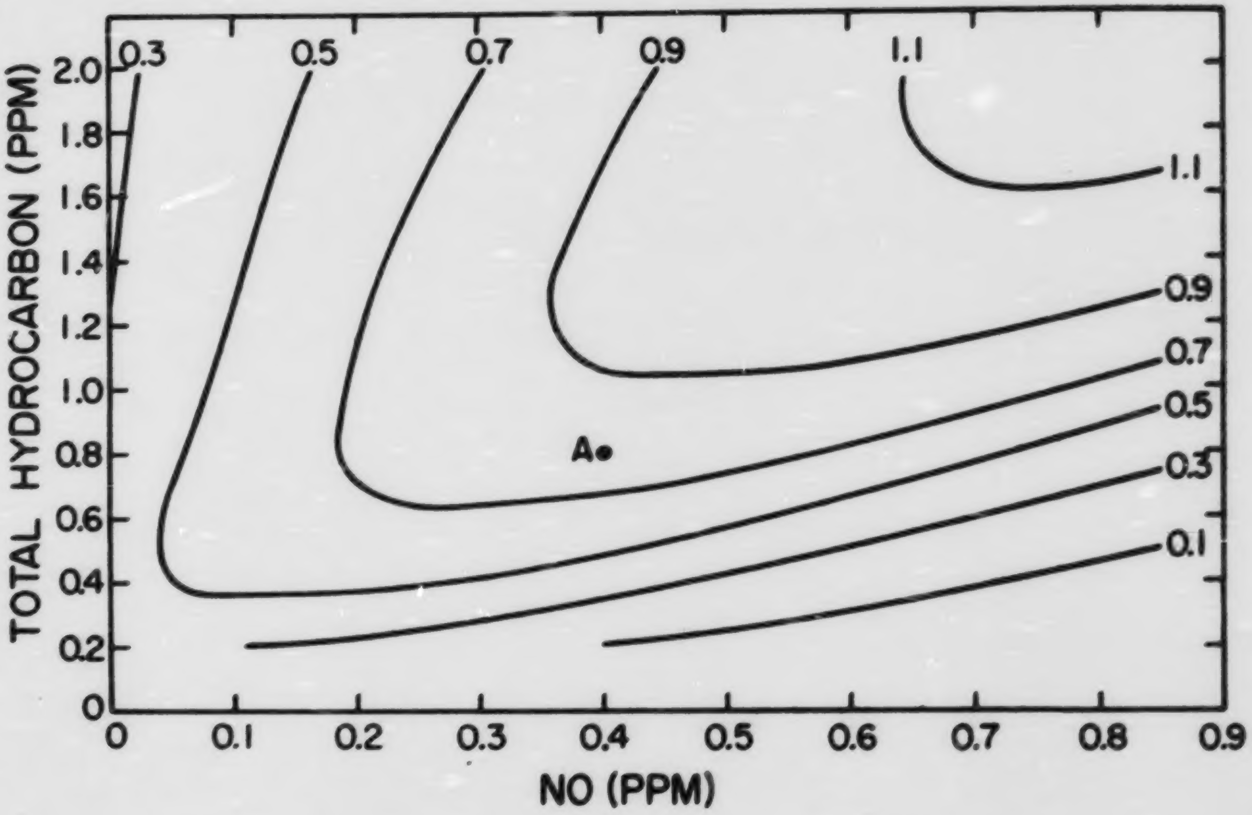

Figure 11. Isopleths of predicted maximum ozone concentration achieved during an 8-hr irradiation of various mixtures of n-butane, propylene, and NO. (Initial concentration of NO_2 equal to 0.1 ppm.)

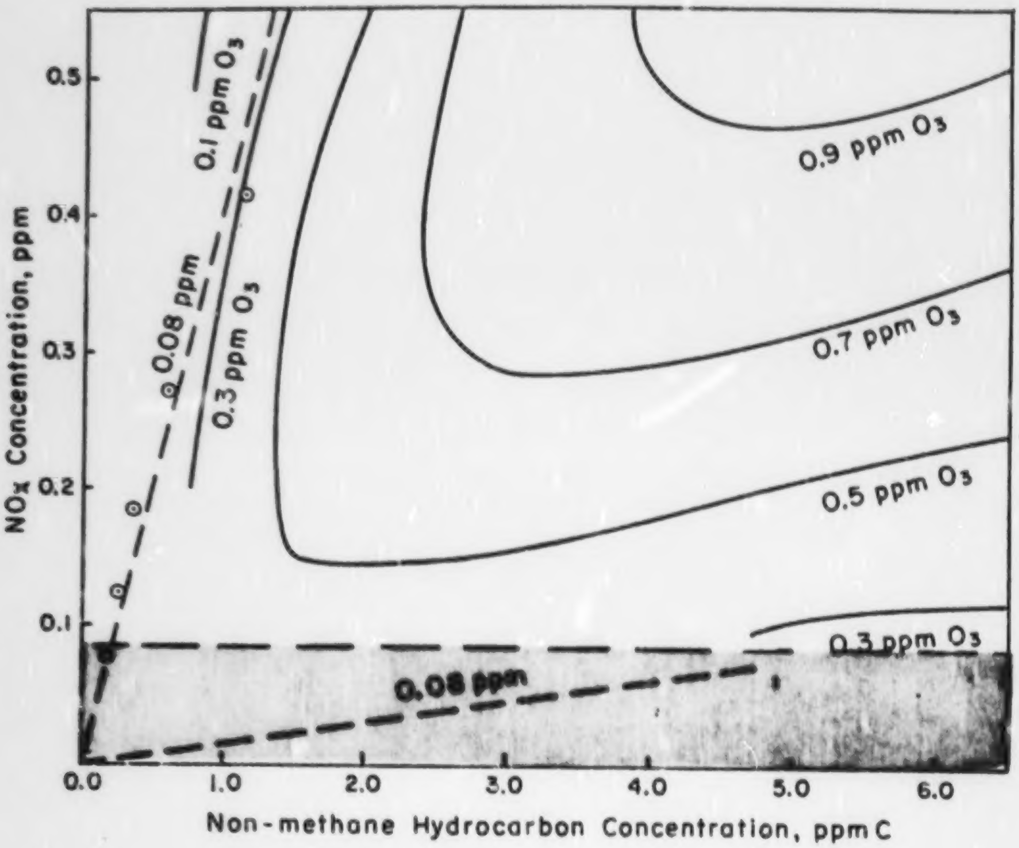

Figure 12. Ozone concentrations for various initial hydrocarbons-NO$_x$ mixtures.
Legend: ——— Calculated values.
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AN ALTERNATIVE TO THE APPENDIX-J METHOD FOR CALCULATING OXIDANT- AND NO_2-RELATED CONTROL REQUIREMENTS

B. Dimitriades*

ABSTRACT

A method is described and offered as an alternative to the Appendix-J method for calculating numerical emission control requirements. The new method is based on the use of oxides/hydrocarbon/nitrogen oxides relationships that were derived from smog chamber data and were expanded using photochemical modeling techniques. Main advantages of the method over the Appendix-J method now in use are the cause-effect nature of the oxides/hydrocarbon/nitrogen relationships used and the quantitative treatment of the nitrogen oxides-precursor role. Disadvantages are the somewhat questionable applicability of the smog chamber data and the method's demand for non-available input information. These advantages and disadvantages and other control-related implications of the method's oxides/hydrocarbon/nitrogen oxides diagrams are discussed.

INTRODUCTION

In the first oxidant control strategy recommended by the United States Environmental Protection Agency (EPA) in 1970, emission control requirements were to be calculated by the well-known Appendix-J method (Figure 1) (1). Briefly, the method is based on use of an "upper limit" curve (Figure 2) relating observed daily maximum one-hour oxidant (O_x) and 6-9 a.m. non-methane hydrocarbon (NMHC) concentrations (2). The Appendix-J method has been known to suffer from several severe limitations -- discussed extensively elsewhere (3) -- and for this reason EPA has been conducting an extensive research program aimed at development of alternative, superior methods.

One product from the research effort is the "smog chamber method" to be described and discussed here. As with the Appendix-J method, the primary purpose of this new method is to estimate the degree of emission control needed for achievement of the national ambient air quality standard (NAAQS) for oxidant/Ozone (O_3). The new method also lends itself to predicting changes in oxidant-related air quality as a result of given emission control. It should be clarified at the outset that the entire method consists of two components used sequentially: One component deals with the dependencies of ambient oxidant/O_3 and nitrogen dioxide (NO_2) on ambient NMHC and nitrogen oxides (NO_x) concentrations; the follow-up component deals with the dependencies of the ambient NMHC and NO_x concentrations on respective emission rates. The procedures

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described and discussed here are addressed to the first component only, that is, to the ambient oxidant/O_3-to-precursor dependencies. Emission reduction is calculated by simply assuming proportional relationships between ambient concentrations and emission rates.

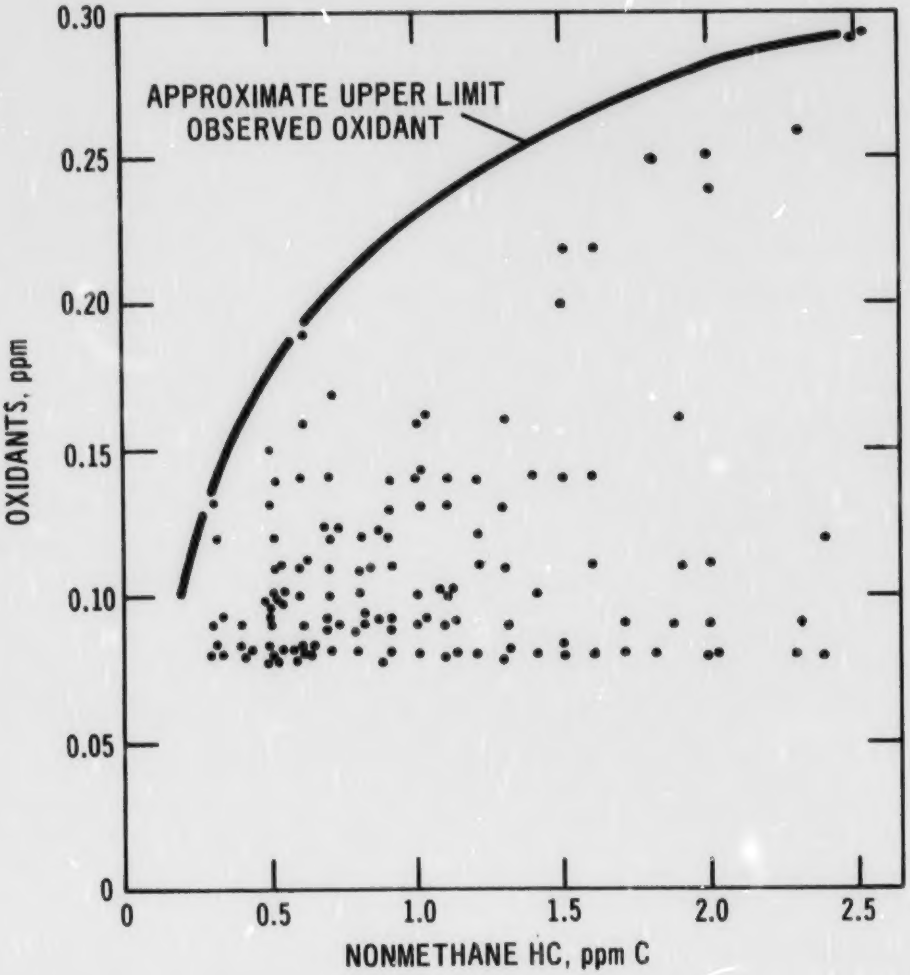

Figure 1. "Upper limit" curve relating ambient maximum one-hour oxidant to 6-9 a.m. concentration of non-methane hydrocarbon.

DESCRIPTION OF THE METHOD

The smog chamber method is based on use of oxides/hydrocarbon/nitrogen oxides (O_3/HC/NO_x) relationships first derived from smog chamber data and subsequently modified to more closely reflect real atmosphere conditions. Therefore, for complete description of the method, it is necessary to describe (a) the underlying smog chamber data and the experimental procedures by which they were obtained, (b) the photochemical modeling techniques used in conjunc-

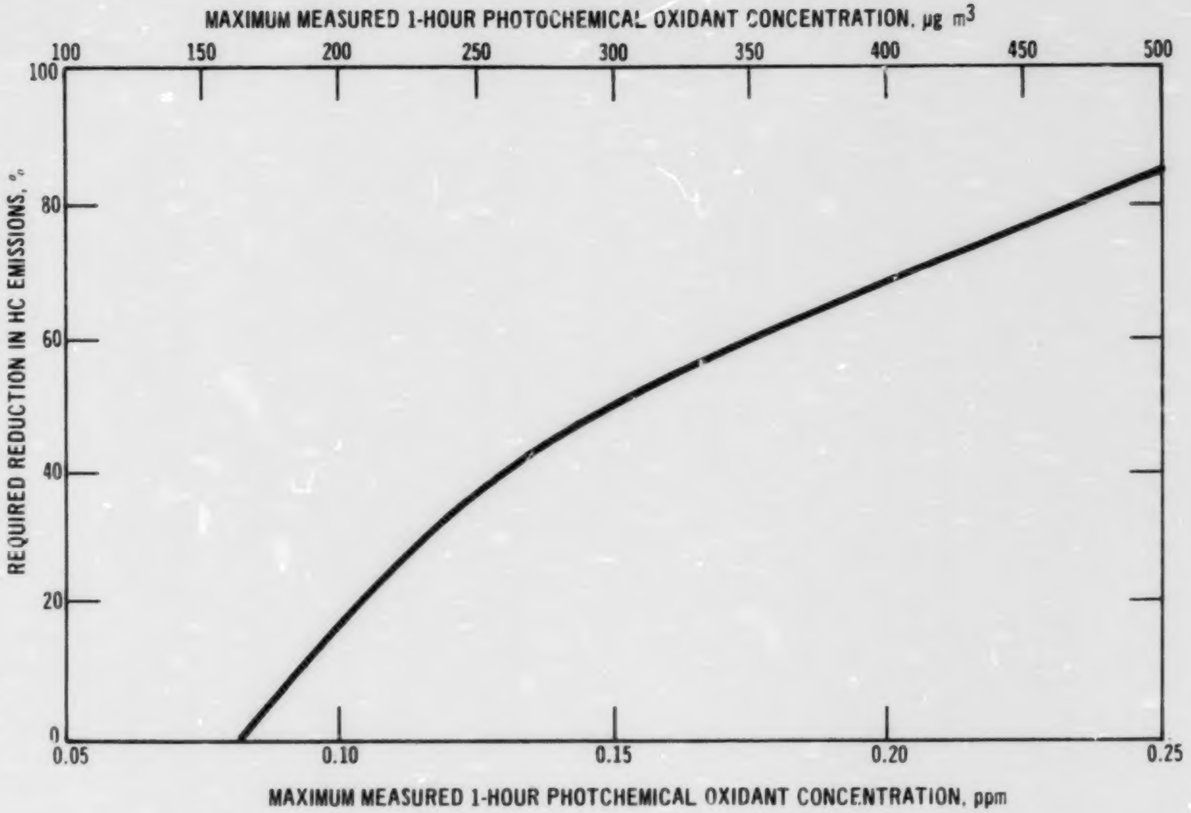

Figure 2. Appendix-J curve relating hydrocarbon control requirements with maximum measured oxidant concentration.

tion with the smog chamber data to derive the requisite O_x/HC/NO_x relationships, and (c) the use of such relationsips to estimate control requirements. The smog chamber data and the modeling techniques are described and discussed elsewhere (4,5,6). The application of these diagrams in calculating control requirements will be described and discussed here.

The O_x/HC/NO_x relationship diagrams used in this method are depicted in Figure 3 in the form of oxidant/O_3 isopleths. For application of these laboratory-derived diagrams to the real atmosphere, it is necessary that the chamber concentrations of oxidant, NMHC, and NO_x be identified or related with the concentrations in the real atmosphere. Such relationships have been assumed here to be as described in the following paragraph.

The highest afternoon concentration of oxidant/O_3 observed in a given region's air is identified with the oxidant/O_3 concentration observed in the smog chamber. Also, the early-in-the-morning (6-9 a.m.) average (during the smog season) NMHC-to-NO_x ratio associated with the observed (real atmosphere) oxidant/O_3 is identified with the NMHC-to-NO_x ratio in the initial chamber charge. Thus, ambient oxidant/O_3 and NMHC-to-NO_x ratio data specify in Figure 3 a single oxidant/O_3 isopleth, and define a constant slope straight line emanating from the origin. The intercept point of these two lines defines the "chamber counterparts" of the ambient NMHC and NO_x concentrations associated with the observed ambient oxidant/O_3 concentration. These "chamber counterpart" concentrations are not expected to be equal to those in the real atmosphere; however the degree of their reduction needed to achieve given degrees of oxidant/O_3 and NO_2 reduction are taken to be equal to the degrees of NMHC and NO_x reduction needed in the real atmosphere.

The detailed procedure for calculating control requirements is illustrated for a hypothetical region, the relevant air quality data for which are given as follows:

- Maximum one-hour oxidant/O_3 in "base" year: 0.40 ppm

- Average 6-9 a.m. NMHC-to-NO_x ratio and 90 % confidence interval during the smog season of the "base" year: 8.0 ± 4.0

- Annual NO_2 mean for the "base" year: 0.06 ppm

Because control requirements depend on the NMHC-to-NO_x ratio, such requirements must be calculated for all ratio values ranging from 4 to 12. Such calculations are illustrated in the following paragraph, using the average ratio value of 8.0.

First, the constant slope line ab is drawn (Figure 3), corresponding to a NMHC-to-NO_x ratio equal to 8.0. The intercept of line ab with the 0.40-ppm-O_3 isopleth defines point e representing the "chamber counterpart" NMHC and NO_x concentrations of 1.57 ppmC and 0.20 ppm, respectively. Next, the NO_x reduction needed for achieving the NAAQS for NO_2 (annual mean of 0.055 ppm) is calculated to be 10 % -- assuming proportionality between 6-9 a.m. NO_x and annual NO_2 mean concentrations. Reducing NO_x by 10 % defines point e' representing 1.57 ppmC of

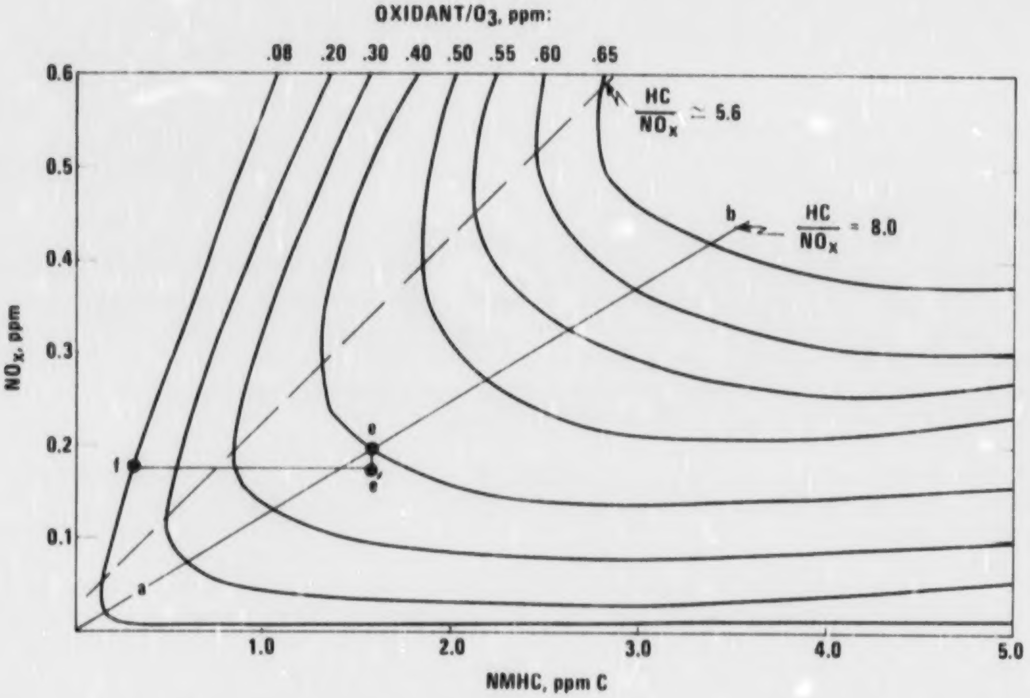

Figure 3. Oxidant/O_3 isopleths derived from combined use of smog chamber and photochemical modeling techniques.

NMHC and 0.18 ppm of NO_x. For achievement of the NAAQS for oxidant/O_3, the NMHC must then be reduced along the line e'f to the point f being the intercept of line e'f with the 0.08-ppm-O_3 isopleth. Such a NMHC reduction is calculated to be 81%

Similar calculations for NMHC-to-NO ratio equal to 4 and 12 give NMHC control requirements equal to 62% and 87%, respectively, the latter figure being the maximum within the given ratio range. It is concluded, therefore, that the control requirement estimates for the given region are 10% for the NO_x emissions and 87% for the NMHC emissions.

DISCUSSION

Points that merit discussion are (a) the strengths and limitations of the new method relative to those of the Appendix-J method, and (b) control implications of the relative roles of the HC and NO_x precursors as such roles are depicted in Figure 3. Since the smog chamber method is offered as an alternative to the Appendix-J method, any judgement to be made upon the new method needs only be a comparative one.

In regard to the conceptual bases, the smog chamber method is advantageous over the Appendix-J method in that it is based on a cause-effect relationship between oxidant/O_3 and the precursors. In contrast, the Appendix-J method is based on a relationship of stochastic nature and therefore its predictions have limited validity. Another major advantage of the chamber method is that it considers and, in fact, permits quantification of the role of the NO_x precursor factor in the oxidant/O_3-forming process. A conceptual limitation of the smog chamber method arises from the fact that the ambient atmosphere cannot be duplicated in the smog chamber. This problem, however, should not be attributed wholly to the chamber method. A part of the problem is caused by the fact that the ambient atmosphere cannot be defined, at least not in terms of commonly available monitoring data. For this reason, any method for predicting air quality will suffer from uncertainties, as direct validation of such predictions is not possible. Another conceptual limitation of the smog chamber method is that although it predicts levels of oxidant/O_3 occurrence, it offers no information whatever on the frequency at which such levels occur. This is a limitation only because the NAAQS for oxidant/O_3 has been defined in terms of a concentration level and a frequency of occurrence.

Aside from its conceptional strengths and limitations, the smog chamber method has strengths and limitations related to its derivation and to its application.

Use of photochemical modeling techniques in the derivation of the method has extended the method's applicability into ranges of precursor concentration and radiation conditions that are known to occur in the real atmosphere, but for which smog chamber data either do not exist or are not reliable. This and other advantages as well as errors/limitations associated with the modeling techniques are discussed in detail elsewhere(6).

Application of the smog chamber method is not as simple as with the Appendix-J method, mainly because it requires more input information. Thus, while both methods require knowledge of the highest (or second highest) one-hour oxidant/O_3 and annual NO_2 mean concentrations for the base year, the smog chamber method needs, additionally, data on the ambient 6-9 a.m. NMHC-to-NO_x ratio. These latter data are not required to be obtained by law; therefore, at present their availability is limited. The requisite data can be obtained through ambient measurements that must be sufficiently abundant to provide a reliable measure of the range of the NMHC-to-NO_x ratio. Thus, it is estimated that a three-month research type effort could provide the requisite minimum amount of aerometric data. In the lack of local ambient data, and provided adequate emission inventory data are available, the average NMHC-to-NO_x ratio can be approximated from such inventory data; the variation around this mean ratio value could be assumed to be equal to the variation measured in other areas of similar pollution characteristics. In the lack of either ambient or emission data, the requisite ratio range could be given rational, assumed values.

Final points of discussion are some implications arising from the diagrams of Figure 3 and pertaining to the relative roles of the HC and NO_x precursors in oxidant formation in atmospheres with unusually high NMHC-to-HC ratios and in rural atmospheres.

The diagrams of Figure 3 were derived from smog chamber data reflecting ambient conditions within a source area (urban area). Based on these diagrams, it appears that the relative roles of the HC and NO_x precursors can be drastically different depending on the air quality goal that must be achieved. Thus, if this goal is the NAAQS for oxidant, 0.08 ppm O_3, then the diagrams indicate that unilateral control of HC is the optimum strategy for achieving the goal, since the degree of NO_x control needed to achieve the same goal is prohibitive. The diagrams further indicate that control of NO_x may have detrimental or beneficial temporary effects but ultimately it is detrimental in that it raises the HC control requirements and, hence, makes achievement of the final goal more difficult.

If the air quality goal to be achieved is relaxed, e.g., to 0.15 - 0.20 ppm O_3 -- these values are used for illustration purposes only -- then unilateral HC control is again an effective control strategy, especially for atmospheres with relatively low NMHC-to-NO_x ratios, namely, lower than 5.0. For such atmospheres, control of NO_x is clearly detrimental. However, for atmospheres with increasingly high NNMH-to-NO_x ratios, NO_x control becomes beneficial. The critical NMHC-to-NO_x ratio beyond which the NO_x role is reversed has not been established, but the overall experimental evidence points to a ratio of 8 to 10, somewhat higher than the value of 5.6 estimated from the diagrams of Figure 3.

With regard to the rural oxidant problem, the evidence now available is not sufficiently complete to permit definition of optimum control strategy. There are several sources of rural oxidant, the relative strengths of which have not been established quantitatively. Transported urban pollutants are almost certain to constitute the major source in rural areas with an oxidant problem (7-11). However, the dependence of such "transported" oxidant on the precursors has not been established. Such dependence, or alternatively the effect of precursor control on rural oxidant, is an extremely complex function of several factors, as explained in the following paragraph.

Based mainly on smog chamber evidence, HC control is expected to have two offsetting effects upon rural oxidant:

- Hydrocarbon control will reduce urban oxidant -- a part of the decrement will be carried into the rural areas during subsequent days.
- Hydrocarbon control will result in greater amounts of NO_x surviving the urban process and being carried into the rural areas. There is evidence to show that the potential for oxidant formation in such "aged" rural air increases with increasing NO_x concentrations (11).

Control of NO_x alone has similar offsetting effects when applied upon urban atmospheres with low NMHC-to-NO_x ratio (<5): (a) it will increase urban oxidant, a part of the increment to be carried into the rural areas, and (b) it will result in rural air with lower NO_x concentration and, hence, with lower potential for oxidant formation. Note, however, that in urban atmospheres with high NMHC-to-NO_x ratio (>10), control of NO_x will reduce oxidant both in the urban and in the downwind rural areas. In conclusion, except for the case of the high NMHC-to-NO_x ratio atmospheres, the net effects HC and NO_x controls upon rural oxidant are neither known nor predictable at this time.

Considering this complexity of the rural oxidant problem and judging from the diagrams of Figure 3, it appears that the most rational emission control strategies at this time are as follows:

1. For achievement of the 0.08 ppm-O_3 air quality standard, the emphasis should be on HC control. The NO_x should be controlled only to the extent needed to meet the NAAQS for NO_2 and/or to prevent ambient NO_x concentrations from increasing as a result of oxidant-reduction.

2. For achievement of a less stringent air quality goal, the optimum strategy depends on the urban NMHC-to-NO_x ratio, namely: (a) for low ratio atmospheres, the strategy should be as in case 1. and (b) for high NMHC-to-NO_x ratio atmospheres, credit should be given to both HC control and NO_x control.

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COMBINED USE OF MODELING TECHNIQUES AND SMOG CHAMBER DATA TO DERIVE OZONE-PRECURSOR RELATIONSHIPS

M. C. Dodge*

ABSTRACT

A method is offered for deriving ozone-precursor relationships that can be used to design a control strategy for urban ozone reduction. The method is derived from the combined results of smog chamber data and photochemical modeling techniques. A model was first developed to fit the maximum one-hour ozone levels obtained in smog chamber studies of irradiated auto exhaust and oxides of nitrogen mixtures. The model was then adjusted to conditions that more closely approximate those of the polluted atmosphere. Included in these adjustments was the use of diurnal values of the photolytic rate constants for the atmospheric pollutants. Based on the modeling results, ozone isopleths were constructed for a wide range of initial pollutant levels. These isopleths can be used to estimate the various combinations of non-methane hydrocarbon and oxides of nitrogen that meet the Federal air quality standard for ozone.

INTRODUCTION

The use of smog chamber data in conjunction with modeling offers a means for estimating the degree of hydrocarbon (HC) and oxides of nitrogen (NO_x) control needed to achieve the air quality standard for ozone (O_3). Chamber data by themselves are not ideally suited for this purpose because of their many limitations. No one chamber study has yielded a sufficient data base to characterize fully all HC and NO_x concentration ranges of interest. Often the irradiation period of the studies is insufficient to determine full O_3 potential of the chamber mixture. Also, smog chambers are normally operated at constant light intensity. The spectral distribution of the light source is often not comparable to that of natural sunlight. In addition, chamber walls can serve as both a source and sink for pollutants; as a consequence, the results obtained from chamber studies may not be applicable to the real world. Modeling complemented with chamber data offers a means of circumventing many of these problems.

The modeling studies presented in this paper were carried out in two stages. In the first stage, a model was developed to fit chamber data of irradiated auto exhaust and NO_x mixtures. In the second stage, adjustments were made to yield a model that is more descriptive of the polluted atmosphere. The adjusted model was used to generate maximum one-hour O_3 concentrations over a wide range of HC and NO_x concentrations. Only the results of the modeling studies will be presented here. A suggested use of these results to design an

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alternative control strategy for urban ozone reduction will be discussed in a separate paper (1).

RESULTS

DEVELOPMENT OF SMOG CHAMBER MODEL

The data base was obtained in the extensive study of irradiated auto exhaust and NO_x mixtures conducted by the Bureau of Mines. In this study, a 100-ft^3 aluminum chamber was charged with dilute auto exhaust mixed with varying amounts of added nitric oxide (NO) and nitrogen dioxide (NO_2). Nonmethane hydrocarbon (NMHC) and NO_x reactants ranged from 0.2 to 5.0 ppmC and 0.08 to 1.4 ppm, respectively. The initial NO_2 concentration was adjusted to approximately 10 percent of the initial NO_x. NMHC-to-NO ratios of the resulting mixtures ranged from 2.3 to 11.6. Chamber contents were irradiated for 6 hours with a mixture of black-lights, blue lamps, and sunlamps. The rate of photolysis of NO_2, K_1, in the chamber was determined to be approximately 0.29 min^{-1}. A complete description of the experimental procedures and results obtained in this study are presented elsewhere (2, 3).

A detailed chemical kinetics mechanism was employed to model the auto exhaust data. The 75-step mechanism contained two HC species: propylene and n-butane. An aromatic hydrocarbon was not included in the model since a reliable mechanism for this class of organics has not been developed to date. A detailed description of the reaction steps included in the propylene and n-butane mechanism can be found elsewhere (4).

The following conditions were used to adapt the model to the Bureau of Mines chamber characteristics:

- k_1 was taken to be 0.32 min^{-1}. This is 10 percent higher than the reported value of 0.29 min^{-1}. Intensity measurements in the chamber were conducted in the first 1 or 2 minutes after switching on the lights. Since the lamps were not fully warmed-up and were, therefore, operating at less than full intensity, the measured k_1 is apt to be low.

- The remaining photolytic rate constants were assigned values corresponding to a solar zenith angle of 60° for a 34°N latitude (Los Angeles). At this zenith angle, k_1 = 0.36 min^{-1}, which is close to the k_1 value reported for the smog chamber.

- The reported (5) chamber dilution rate of 2.3 percent per hour and the half-life of O_3 in the dark of 14 hours were used in the model.

- The initial nitrous acid (HONO) concentration was taken to be 6 X 10^{-4} ppm. This value reflects the formation of HONO, from the thermal reaction of NO, NO_2, and water (H_2O), occurring in the period between injection of the reactants and onset of irradiation.

- To simulate "dirty" chamber effects (6), the chamber walls were assumed to be a source of propylene. A reaction was included in the model to allow propylene to desorb continually from the chamber surfaces at a rate of 1 X 10^{-4} ppm min^{-1}. This rate reproduced the high O_3 yield obtained in a chamber run containing only background levels of HC (<0.1 ppmC) and 0.081 ppm NO_x.

- The reported initial concentration of formaldehyde (HCHO) was included in the model. Acetaldehyde was taken to represent the remaining aldehyde content of the auto exhaust sample. Its molar concentration was assumed to be two-thirds of the initial HCHO concentration.

Seventeen experiments were modeled in this study. The one adjustable parameter used to achieve a fit to the data was the relative concentration of initial n-butane and propylene. The closest fit to the experimental data was obtained when the auto exhaust mixture was assumed to contain 75 percent n-butane and 25 percent propylene on a ppmC basis.

The "goodness of fit" was determined by comparing the simulated profiles for NO_2 and O_3 to the experimentally generated profiles. The agreement between the experimental maximum one-hour O_3 concentration and the simulated value for each of the runs is given in Table 1. The chamber data were reported in terms of total non-NO_2 oxidant (7) measured with a Mast meter (and corrected for NO_2 interference). Such oxidant was estimated to consist of about 90 percent O_3 and 10 percent non-O_3. The experimental O_3 values listed in Table 1 are, therefore, 90 percent of the reported maximum one-hour average oxidant concentrations. The first entry in Table 1 corresponds to the chamber run containing only background levels of hydrocarbons discussed earlier.

In general, the experimentally determined maximum one-hour O_3 levels and the predicted values are in good agreement. On the average, there is a 14 percent difference between the experimental and simulated results for these 17 runs. The lack of agreement is most pronounced for Runs No. 1 and 2. The poor fit for these runs, however, is deceptive. The high NO_x concentration in Run No. 1 inhibited O_3 formation to the extent that, after 6 hours when the experiment was terminated, O_3 was just beginning to appear. Under such conditions, the results are extremely sensitive to any small difference between the experimental and predicted induction periods. The model predicts a slightly greater induction period than was observed. It is expected that agreement would have been much closer if the chamber contents had been irradiated until the O_3 maximum was reached. Run No. 2 contained an exceedingly low HC concentration and, consequently, this run was highly affected by chamber contamination. In this experiment, the "dirty" chamber effect on O_3 production was as important as the initial reactant parameters. The poor agreement between the experimental and simulated results probably reflects the inability of the model to treat chamber artifacts accurately. If Runs No. 1 and 2 are excluded, the simulated results for the remaining 15 runs are in error by an average of only 10 percent. The experimental error associated with the smog chamber itself is at least as great as this. Seven replicate runs were carried out during this chamber study. The average difference in the maximum one-hour O_3 concentrations for each of these pairs of runs was 15 percent.

TABLE 1. COMPARISON OF CHAMBER DATA AND MODEL PREDICTIONS

				Max 1-hour Ozone[†]		
No.	NMHC/NO_x	NMHC[*]	NO_x[†]	Expt.	Calc.	Percent Error
X	<1.2	<0.1	0.081	0.025	0.025	-
1	2.3	1.45	0.618	0.073	0.041	44
2	2.5	0.187	0.075	0.118	0.075	36
3	2.5	0.656	0.265	0.103	0.088	15
4	3.3	0.92	0.276	0.141	0.166	18
5	5.1	0.415	0.083	0.188	0.151	20
6	5.1	4.80	0.046	0.425	0.458	8
7	5.1	1.403	0.272	0.240	0.247	3
8	5.3	0.657	0.125	0.207	0.176	15
9	5.3	2.12	0.398	0.323	0.340	5
10	7.3	0.97	0.133	0.199	0.222	12
11	7.4	4.75	0.641	0.558	0.539	3
12	7.6	3.14	0.414	0.458	0.432	6
13	8.3	2.13	0.256	0.355	0.343	3
14	11.4	3.21	0.281	0.373	0.393	6
15	11.4	0.95	0.083	0.252	0.194	23
16	11.5	4.79	0.416	0.623	0.4[illegible]	21
17	11.6	2.13	0.183	0.332	0.308	7

[*] Units of ppmC

[†] Units of ppm

DEVELOPMENT OF ADJUSTED MODEL

In order to relate O_3 formation to HC and NO_x emissions, it is first necessary to adjust the smog chamber model to conditions that are more representative of the polluted urban atmosphere. The smog chamber model described above is not suitable for predicting ambient O_3 concentration for several reasons:

- The present model treats chamber artifacts, such as wall degassing of propylene, that have no counterpart in the atmosphere.
- The chamber contents were irradiated for only 6 hours. The light intensity for this period of time in the chamber is substantially less than the integrated light intensity for a 10-12 hour period on a typical summer day. Of the 17 chamber runs modeled in this study, only 6 (Runs No. 11, 12, 14-17) reached an O_3 maximum during the 6-hour irradiation. O_3 was still on the rise in the remaining runs when the experiments were terminated. Thus, in most of these runs, the potential for O_3 production is greater than what was observed.

- The chamber runs were conducted at constant light intensity in contrast to the diurnal variation of natural sunlight.

- The initial ratio of NO_2 to NO_x varied considerably from run to run and was most pronounced for the low-NO_x experiments. Such variation can have a marked effect on the maximum one-hour O_3 level and makes comparison of the data difficult.

The following adjustments were made to the smog chamber model in an effort to generate a model more representative of the urban environment:

- No initial concentration of HONO was assumed.

- Wall degassing of propylene, used to simulate the effects of chamber contamination, was deleted.

- Wall degradation of O_3, used to describe the dark decay of O_3 in the chamber, was deleted.

- The initial NO_2 concentration was taken to be 25 percent of the initial NO_x.

- Diurnal one-hour average values of the photolytic rate constants were used. These rate constants, as a function of solar zenith angle for the Los Angeles summer solstice, were obtained from a computer routine developed for this purpose (8).

- Simulations were carried out for a nine-hour period corresponding to the hours between 7 a.m. and 4 p.m. Implicit in this treatment is the assumption that full atmospheric loading has occurred by 7 a.m. and that no influx of fresh pollutants occurs in the subsequent nine-hours.

- A "worst case" approach was adopted to describe the dispersion of pollutants. A zero wind speed was assumed and the only dispersion of pollutants considered was that caused by the daily lifting of the inversion layer. The worst mixing occurs along the West Coast where there is only a 100-meter difference between the mean summer morning and afternoon mixing heights (9). Over a nine-hour period this corresponds to a three percent per hour dilution rate.

Using the adjusted model, simulations were carried out for initial NMHC concentrations of 0.10 to 5.0 ppmC and NO_x of 0.005 to 0.6 ppm. The maximum one-hour O_3 levels obtained in these simulations as a function of NMHC at constant NO_x are shown in Figure 1.

The plots in Figure 1 were used to determine the various combinations of NMHC and NO_x concentrations that correspond to the air quality standard for O_3 of 0.08 ppm. These values were used to generate the O_3 isopleth shown in Figure 2. The shaded area depicts the various combinations of NMHC and NO_x that are predicted to meet the O_3 standard.

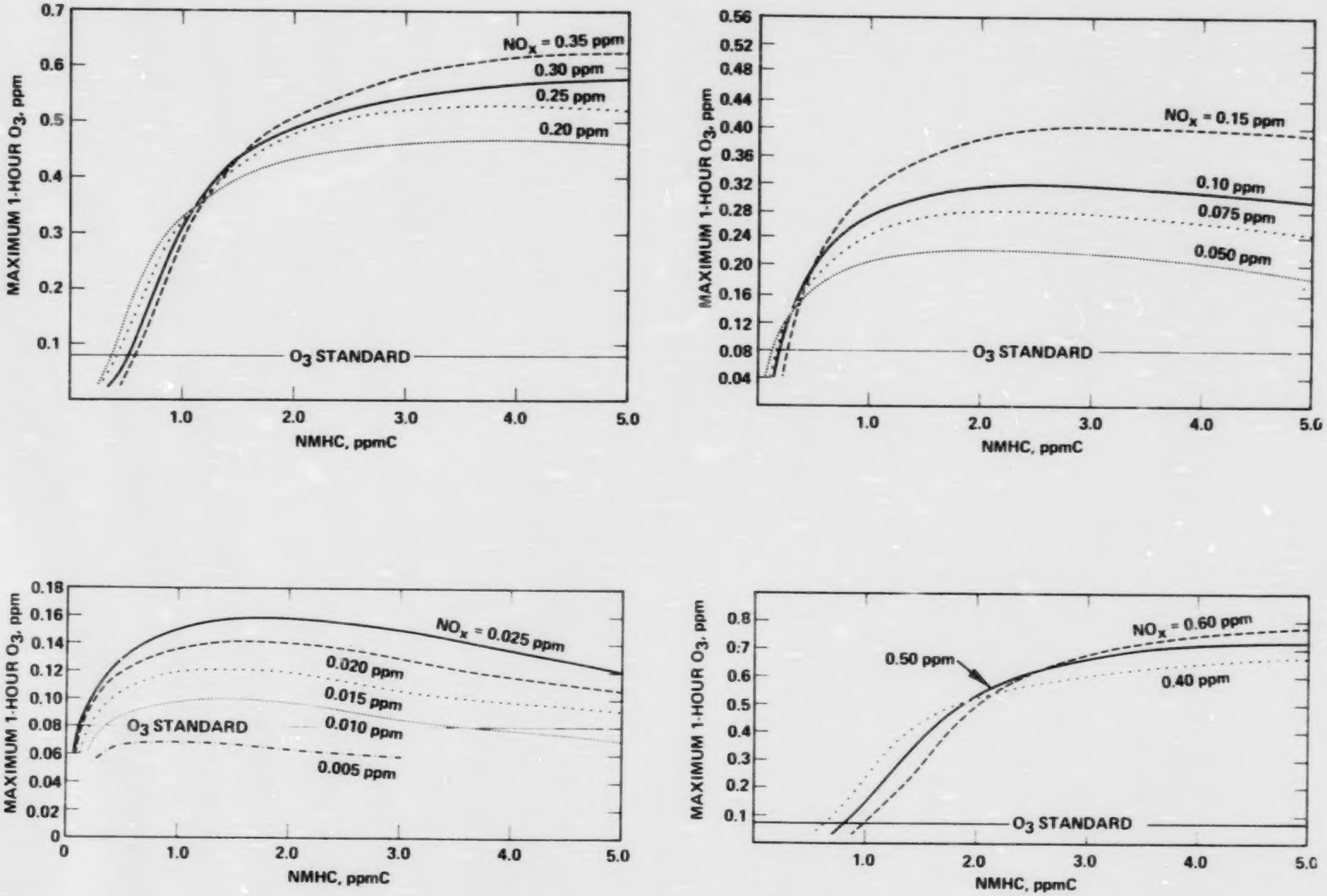

Figure 1. Maximum one-hour O_3 as a function of NMHC at various NO_x levels.

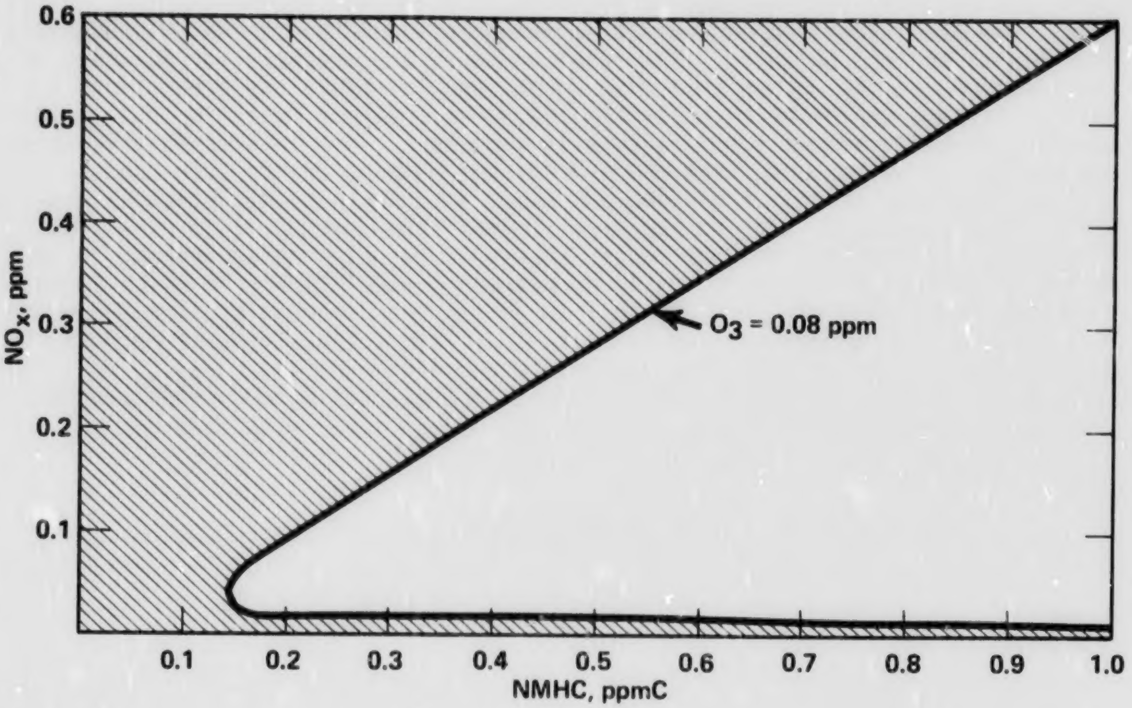

Figure 2. Ozone isopleth corresponding to the Federal standard of 0.08 ppm.

Following this procedure, a series of O_3 isopleths was constructed that correspond to various maximum one-hour O_3 values between 0.08 and 0.65 ppm. These isopleths are shown in Figure 3. A line corresponding to a NMHC-to-NO_x ratio of 5.6 is drawn through the apex point of these isopleths. This line divides the figure into a region that is predominantly NO_x-rich and one that is predominantly HC-rich. In the low HC/NO_x region to the left of the line, a reduction in HC levels will result in the greatest decrease in O_3 yields. In contrast, throughout most of the high HC/NO_x region to the right of the line, a reduction in NO_x levels will lead to the greatest decrease in O_3 formation.

CONCLUSIONS

The O_3 isopleths constructed in this study can serve as a basis for developing a control strategy for the Los Angeles area. Using appropriate diurnal photolytic rate constants and pollutant dispersion rates, similar isopleths can be generated for other localities. Thus, with this method it is possible to develop specific control strategies for individual areas of the country.

The accuracy of the results presented in this paper depend on both the validity of the chamber data used to develop the model and the uncertainties contained in the model itself. The error associated with precision for the chamber data appears to be only about 15 percent. The errors resulting from "dirty" chamber effects and other chamber artifacts, however, may be significant. The model itself also contains a number of uncertainties and assumptions that may or may not be valid. The rate constants and products for a number of the reactions in the mechanism are in doubt, and therefore the predictions are subject to some degree of uncertainty (10). The greatest source of uncertainty, however, probably arises from the simplifying assumptions invoked in developing the model. It was assumed that the hydrocarbon content of the auto exhaust mixture consisted of only propylene and n-butane. Such an assumption is probably valid since good fits to the experimental data were obtained with this simplistic representation. The model, however, was only tested against chamber runs with an initial HC-to-NO_x ratio of between 2 and 12. Within this limited range the model does give acceptable fits to the experimentally generated ozone. However, the simulations carried out for HC/NO_x of much less than 2 or much greater than 12 are subject to a higher degree of uncertainty. Thus, the extreme upper left and lower right portions of Figure 3, which correspond to very low and very high HC-to-NO_x ratios, should be viewed with caution.

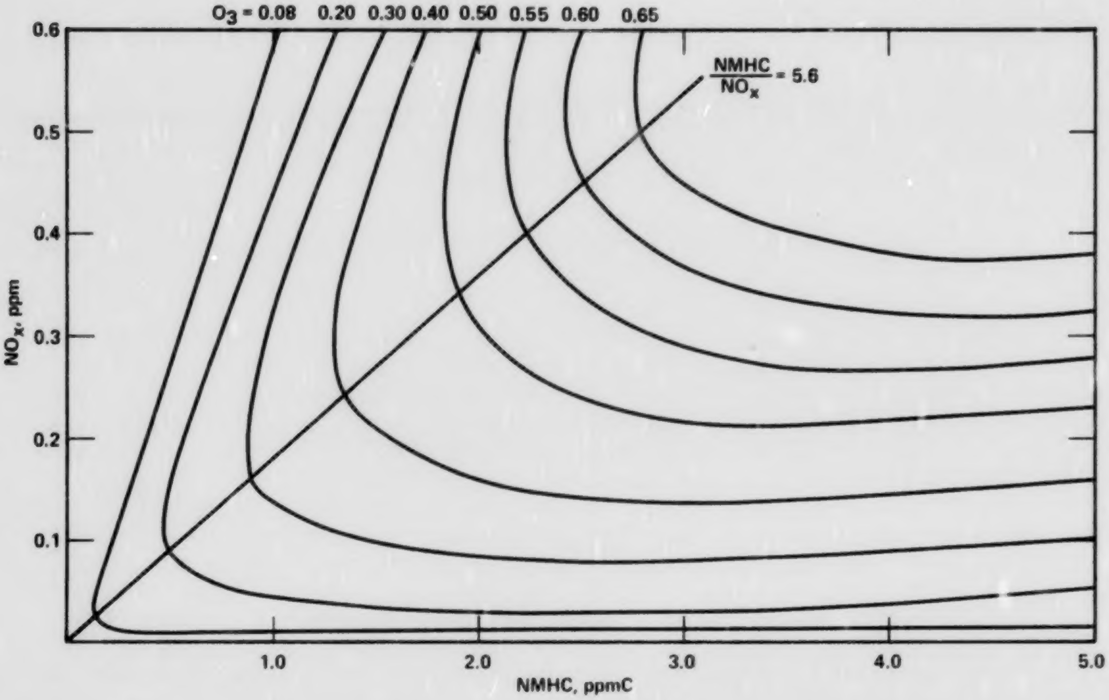

Figure 3. Ozone isopleths corresponding to maximum one-hour O_3 concentrations.

Questions may also be raised about how representative the adjusted model is in relation to the real-world situation. For the simulations carried out in this study, the atmosphere was treated as if it were a static chamber, with full loading of pollutants shortly after sunrise and no further influx or fresh pollutants during the day. Such a situation clearly does not conform to the real world. The adjusted model, however, was designed with the intent of describing a "worst case" condition for the atmosphere. By assuming stagnant conditions, early loading of pollutants, clear skies, and no influx of fresh sources of NO that might tend to reduce O_3 levels, the most favorable conditions for O_3 formation it is hoped, were established. Thus, the maximum one-hour O_3 concentrations predicted by the model are apt to be higher than those that would be found routinely in the atmosphere given comparable 6 - 9 a.m. levels of NMHC and NO_x. Such an approach is consistent with the existing air quality standard for O_3, which is expressed in terms of an hourly average not to be exceeded more than once a year.

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OUTDOOR SMOG CHAMBER STUDIES: EFFECT OF DIURNAL LIGHT, DILUTIION, AND CONTINUOUS EMISSION ON OXIDANT PRECURSOR RELATIONSHIPS

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ABSTRACT

The influence of diurnal light intensity, dilution, continuous injection, and combinations of these on the Dimitraides' Smog Chamber Method for Oxidant Control calculations is examined using experimental data from the University of North Carolina outdoor chamber. Factors influencing the relative speed of the photochemical system (heterogeneous process, photoacceptors other than nitrogen dioxide, and nitrogen dioxide to oxides of nitrogen ratio) can change ozone by 20 percent under diurnal light conditions. Experimental data suggest that dilution of a reacting system will have less than proportional effect on ozone formation. Experiments comparing static conditions with continuous injection of the same mass into the same volume over 12-hour periods showed that the ozone profiles were similar. Maximum ozone in dynamic experiments was 90 percent of ozone in static experiments when the total mass of oxides of nitrogen and hydrocarbon was the same. Similar results occurred in experiments with simultaneous injection and dilution.

INTRODUCTION

A method for calculating control requirements based on smog chamber data has been proposed by Dimitriades (1). The original data base consisted of constant light-intensity, static experiments in the Bureau of Mines smog chamber. Through the use of modeling, these results have been extended by Dodge (2) to values not originally included and for a single diurnal-light-intensity pattern with certain chamber characteristics removed. The purpose of this paper is to use data from the University of North Carolina (UNC) outdoor smog chamber to address some factors related to the use of static smog chamber results in estimating control requirements. Three general factors will be discussed: (a) diurnal and seasonal light intensity variations, (b) dilution of reactant system, and (c) continuous injection of reactants.

CHAMBER AND INSTRUMENTS

The UNC dual outdoor chamber (3) is constructed of 5 mil (127 μm) FEP Teflon film supported by an exterior wooden A-frame. It is divided into two compartments, each 148 m^3. The interior surface is 98% Teflon and 2% aluminum

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and glass. The chamber operates with natural sunlight, temperature, and humidity, and the air source is natural rural background air of very low reactivity. In normal chamber operation, the rural background air was not pretreated; in some experiments, however, it was filtered by activated charcoal. Ozone (O_3) is measured by chemiluminescent reaction with ethylene using O_3-nitric oxide (NO) gas-phase-titration for calibration. NO and oxides of nitrogen (NO_x) are determined by chemiluminescent reaction with O_3. Nitrogen dioxide (NO_2) is determined by difference.

LIMITATIONS

The NO_x meter is subject to interference by other nitrogen compounds. Comparison tests of the NO_x meters used suggested that the primary interfering compound in the sampling arrangement was peroxyacetylnitrate (PAN), and that there was essentially no response to nitric acid (HNO_3) even though measurements by the Battelle subtractive method showed that HNO_3 was present at the expected concentration (3). Interference in urban hydrocarbon (HC) mix experiments by PAN is 5-10% of the initial NO_x at the end of the run since only low concentrations of PAN are formed. In addition, one of the three NO_x meters exhibited a 25 ppb positive interference for NO after NO_2 maximum. It has subsequently been shown that this was a problem in the detector housing. Data obtained with this meter are uncorrected and thus do not obey photostationary state (PPS) for NO, NO_2, O_3 after NO_2 maximum; data from other meters appear to obey PPS to within the limits of the meter.

Like any smog chamber, there are potential wall effects which may influence the reaction system. Modeling studies, however, suggest that the UNC chamber has rather low rate constants for the heterogeneous reactions that form nitrous acid ($NO + NO_2 + 2H_2O \rightarrow 2HNO_2$) and nitric acid ($N_2O_5 + H_2O \rightarrow 2HNO_3$). These reactions are the two most important surface-mediated processes in most mechanisms. The nitrous acid (HNO_2) can cause a rapid irritation of the reaction system and the formation of HNO_3 increases the rate of removal of NO_2 after O_3 formation occurs. On the other hand, some results could be explained by assuming that the walls may contribute small amounts of NO_x during hot midday portions of runs. The mechanism by which nitrate on the walls may be recycled to NO_2 is not known.

RESULTS

DIURNAL LIGHT INTENSITY

The primary effect of diurnal light intensity conditions is to set a limit on the duration of a photochemical system and therefore, in those systems that do not completely consume NO_2, a limit on the amount of O_3 which can be produced. At the UNC chamber location, the length of a solar day varies from 9 hours 34 minutes in December to 14 hours 25 minutes in June. The maximum total solar radiation intentisy for totally clear days varies from 0.6 $cal\text{-}cm^{-2}\text{-}min^{-1}$ (approximately 0.2 to 0.55^{-1} for Φk_a for NO_2 photolysis). Many indoor smog chamber runs are of much shorter duration at less than optimum light-intensity conditions and thus the O_3 isopleths produced are often a function of the time of irradiation.

In diurnal light intensity experiments, each set of initial conditions of HC and NO_x has its own unique photochemically weighted light-history. Factors that affect the relative speed of a HC-NO_x system, such as a large source of HNO_2 initially present, the presence of other photoacceptors (aldehydes), or high NO_2-to-NO_x ratios, can cause an increased yield in O_3 because the system can reach O_3-forming potential during maximum light intensity. In the UNC outdoor chamber, side-by-side comparison of static runs, with all initial conditions the same except for the addition of acetaldehyde, (at 10% of the non-methane hydrocarbons (NMHC) can yield a 20% increase in O_3. Increasing the NO_2-to-NO_x ratio from 0.2 to 0.4 at 0.36 NO_x and 3.4 ppmC can yield a 20% increase in O_3. The systems producing higher O_3 under the above conditions are faster: the NO-NO_2 crossover and NO_2 maximum occur up to 1.5 h earlier in the solar day, and O_3 formation starts earlier.

In extrapolating chamber results to the open atmosphere, (for instance by a modeling technique), it is important to choose not only the length of a solar day and its maximum intensity appropriate for the time period of desired control, but also to choose a correct relative speed. That is, the concentration of photoacceptors other than NO_2 and an NO_2-to-NO_x ratio that will lead to a proper time scale of events must be specified. Little information is available regarding the relative speed of the open atmosphere. The heterogeneous contribution to HNO_2 formation may be small. Aldehydes are usually present which decrease the role of HNO_2. It is difficult to estimate how much NO is oxidized thermally at high concentrations before it can be diluted to ambient concentrations.

Based on UNC experiments, it is estimated that for a given diurnal light intensity profile, these factors can lead to 20% variation in the location of O_3 isopleths. Changing light intensity profiles from one season to another can lead to large changes (> 50%) in locations of O_3 isopleths.

DILUTION

In a photochemical system, over a short time period, NO, NO_2, and O_3 are nearly in photoequilibrium, since other competing reactions are usually much slower than the classic photostationary state reactions. Over a long time period, however, free radicals compete quite successfully for NO, thereby increasing the O_3. That is,

$$[O_3] \approx \frac{\Phi k_a}{k_3} \frac{[NO_2]}{[NO]}$$

where $[NO_2]/[NO]$ is a function of radical flux (organic reactions). As a first approximation, as long as the absolute photolysis rate of NO_2 is large enough, dilution should not affect the O_3, because dilution would not change the NO_2-to-NO ratio. The formation of O_3 is essentially a first-order process, while destruction of O_3 is a second order process; therefore, dilution could potentially have a greater affect on the O_3-destructive processes leading to higher O_3 yields per precursor molecule. The oxidation of NO to NO_2 by free radicals can be approximated by a first order process to the extent that the free radicals are in steady-state. Therefore, the effect of dilution depends upon how dilution effects the free-radical-NO-oxidizing species which are at very low concentration in near steady-state.

Figure 1 shows the results of dilution on a relatively slow NO_x-synthetic urban mix dual run in the UNC chamber. The dilution rate was 9.5%$^{-1}$, a rate slightly less than the NO-to-NO_2 oxidation rate, as evidenced by the slow rise in NO_2 on the diluted side. Two processes, both acting to lower the concentration, were operating on NO: dilution and conversion to NO_2. Dilution also acted to lower NO_2, but conversion of NO to NO_2 maintained or actually increased the NO_2 concentration; therefore, a more optimum NO_2-to-NO ratio was achieved earlier in the solar day. Ozone was therefore formed at a faster rate in the diluted side than in the undiluted side which did not achieve optimum O_3-producing conditions until later in the solar day when the light intensity was decreasing. Apparently, this dilution rate did not greatly influence the free-radical concentrations responsible for NO-to-NO_2 conversion.

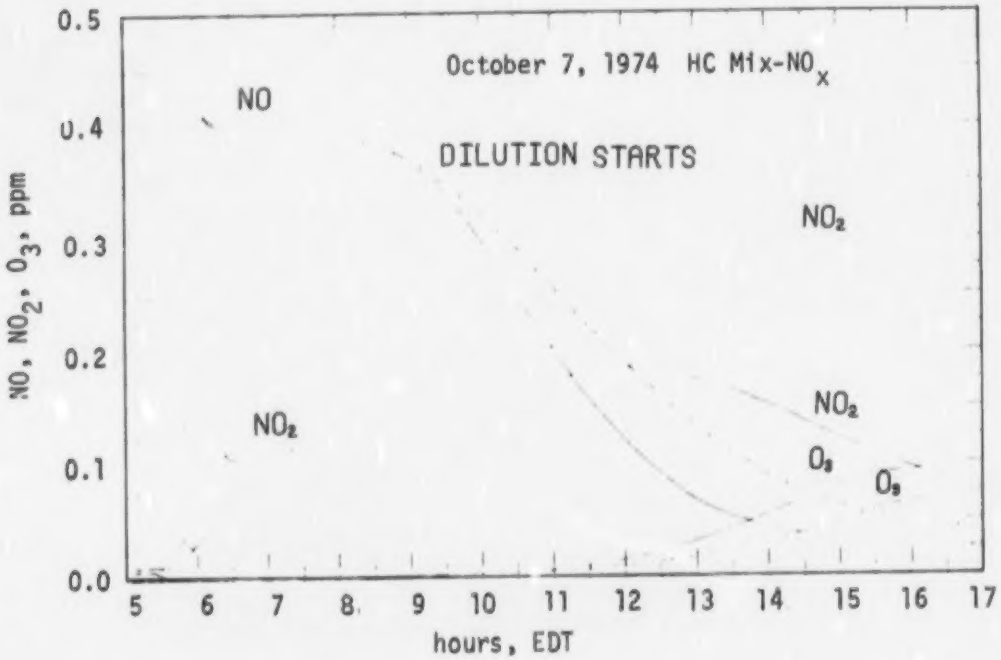

Figure 1. Dual run comparing dilution and no dilution. Initial conditions: NOx (—) 0.504, (--) o.512 ppm; NO_2 (—) 0.106, (--) 0.111 ppm; NMHC (—) 2.39, (--) 2.43 ppmC urban hydrocarbon mix in the UNC outdoor smog chamber. Dilution rate 9.5% per hour.

This experiment has been duplicated and experiments have been performed at other conditions. In those experiments, dilution rates close to the NO-to-NO_2 conversion rate made more O_3 by dilution, and higher rates made less O_3. (Unfortunately, the NO_x meter which exhibited NO interference was used in these experiments so the fact that the system may have obeyed PSS at the end is not evident.)

Another experiment in the UNC Aerosol Chamber (Figure 2), illustrates how difficult it may be to dilute O_3. The normal run was over by 1200 EDT, and the chamber was exhausted. Although "NO_x" and NO decreased at a very rapid rate ($50\%h^{-1}$) O_3 did not decrease until more than one hour of dilution had occurred, and then the decrease was not proportional to the dilution rate.

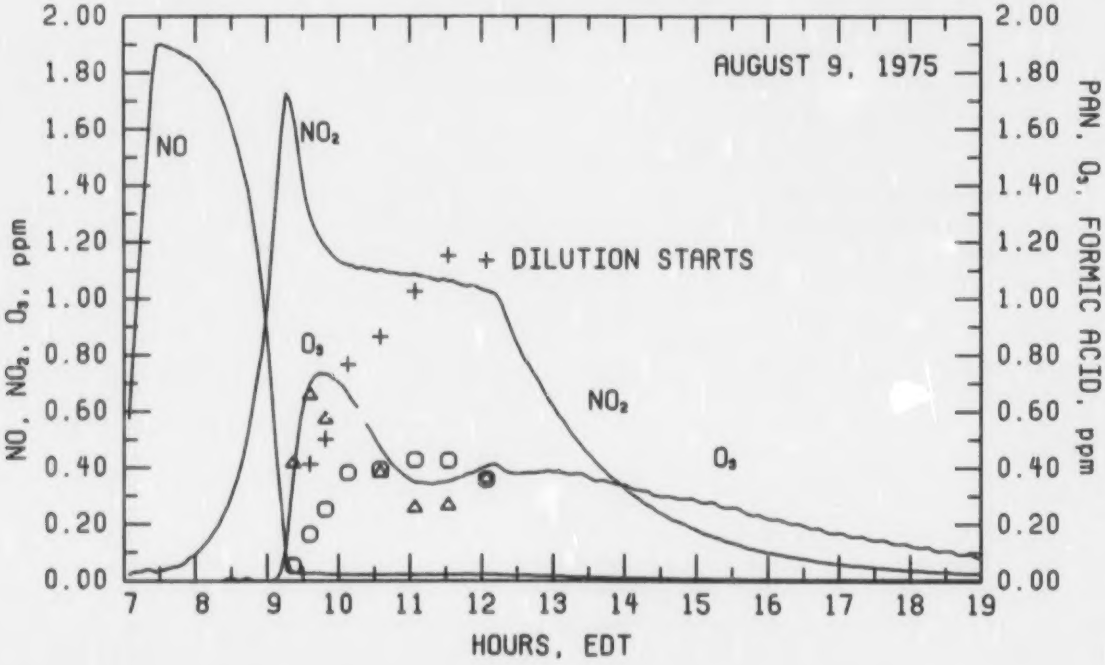

Figure 2. Effect of dilution in a high concentration run. Initial conditions: NOx, 1.95 ppm; NO_2, 0.05 ppm; propylene, 23.3 ppmC in UNC outdoor aerosol chamber.

These and other experiments would suggest that dilution may have substantially less impact on O_3 formed in photochemical systems than one might predict. Dilution patterns of the type discussed here are not very typical of urban atmospheres. The effects of dilution and continuous emission will be discussed subsequently.

CONTINUOUS EMISSION

In a typical urban environment, reactant material is usually emitted throughout the day. The volume into which the reactants are mixed determines the concentration of precursors available for O_3 formation. Static smog chamber experiments, on the other hand, start with all the mass present initially.

The UNC dual chamber has been used to compare static experiments with those in which the same mass was added to the same volume, but ramp-injected slowly over a 12 hour time period (0600-1800 EDT). In these experiments, propylene, a 60:40 mixture of n-butane:propylene, and the UNC mix (acetylene, 5 paraffins, 6 olefins) were each used as a HC. All static experiments had a NO_2-to-NO_x initial ratio of 0.2. On the ramp side, NO and HC were injected each minute. Between 5 and 10% of the NO was oxidized to NO_2 at injection.

Figures 3-5 illustrate some typical results. (Solid lines are static, dashed lines are ramp). Table 1 summarizes the conditions and results. In general, the O_3 profiles in the static-and ramp-injected runs are very similar. The ramped side usually forms O_3 earlier and is higher in O_3 until afternoon, when the static side usually overtakes and slightly passes the ramped O_3. The O_3 at 1900 EDT in the ramped run is usually about 90% of the static O_3 unless cloud conditions in the late afternoon influence the final O_3 (these have a slightly lower percentage). In two runs, the ramped side formed more O_3. This was apparently because of a low NO injection rate, resulting in less total NO and a shift in the HC-to-NO_x ratio on the ramped side, compared to the matching static run.

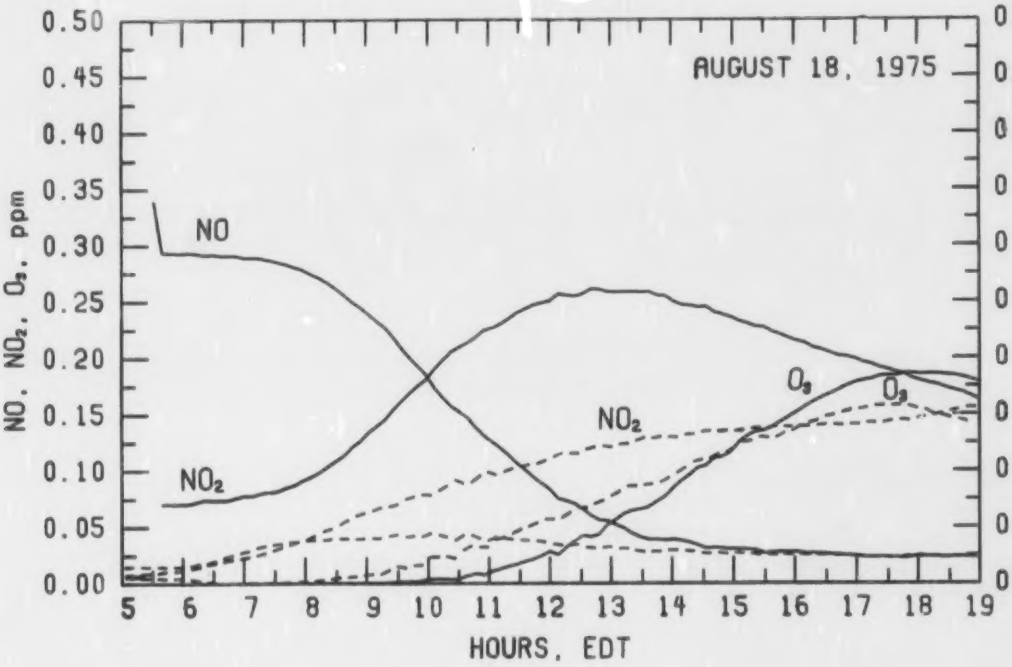

Figure 3. Static (—) and Ramp (--) injection dual run in UNC outdoor smog chamber. Initial conditions at 0545 in static side (—): NO, 0.29 ppm; NO_2, 0.07 ppm; n-C_4H_{10}, 0.60 ppmC; C_3H_6, 0.40 ppmC. Ramp side (--) would achieve: NO, 0.36 ppm; n-C_4H_{10}, 0.60 ppmC; C_3H_6, 0.40 ppmC at 1800 hours if no reaction occurred.

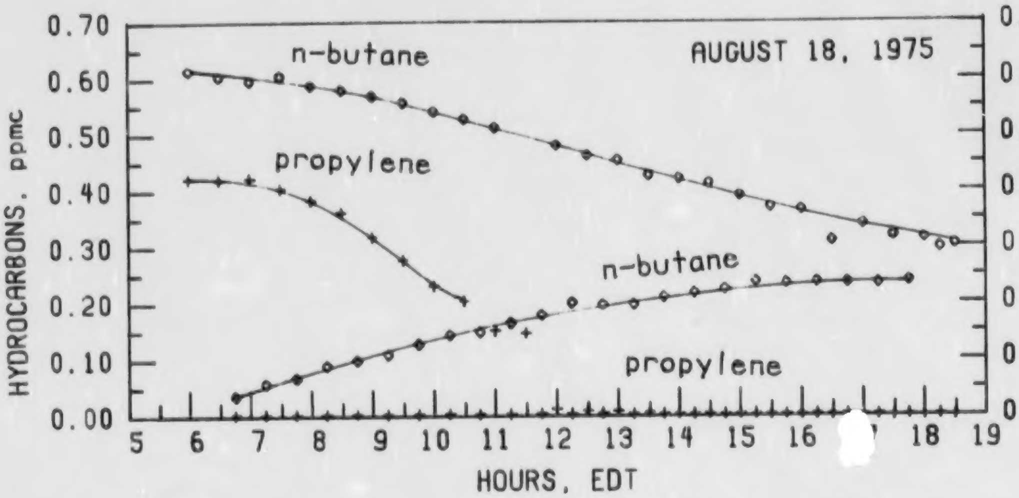

Figure 4. Static (—) and Ramp injection (--) dual run in UNC outdoor smog chamber. Initial conditions at 0545 in static side (—): NO, 0.29 ppm; NO_2, 0.07 ppm; n-C_4H_{10}, 0.60 ppmC; C_3H_6, 0.40 ppmC. Ramp side (--) would achieve: NO, 0.36 ppm; n-C_4H_{10}, 0.60 ppmC; C_3H_6, 0.40 ppmC at 1800 hours if reaction occurred.

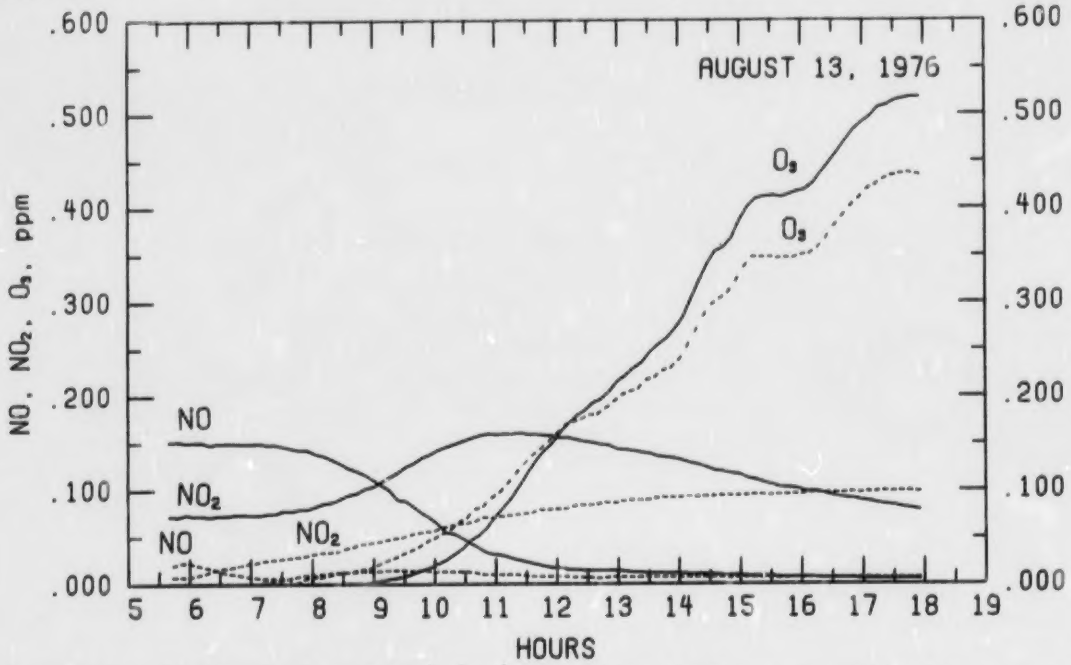

Figure 5. Static (—) and Ramp (--) injection dual run in UNC outdoor smog chamber. Initial conditions at 0540 in static side: NO, 0.151 ppm; NO_2, 0.072 ppm; 1.93 ppmC urban hydrocarbon mix. Ramp side (--) would achieve: NO, 0.22 ppm; 1.93 ppmC urban hydrocarbon mix at 1800 hours if no reaction occurred.

TABLE 1. OZONE FORMATION IN STATIC AND RAMP INJECTED OUTDOOR SMOG CHAMBER EXPERIMENTS

Date	Precursor Conditions[a] NO_x	Precursor Conditions[a] HC	cmp[b]	HC/NO_x ppmC/ppm	O_3 max, ppm static	O_3 max, ppm ramp	ramp/static %
8/16/75	0.37	0.98	P	2.65	0.68	0.48	71
8/17/75	0.36	1.00	B/P	2.78	0.28	0.25	89
8/18/75	0.36	1.00	B/P	2.78	0.18	0.16	89
8/4/76	0.35	0.97	M	2.70	0.05	0.05	100
8/5/76	0.31	1.93	M	6.23	0.24	0.32[c]	133
8/6/76	0.24	0.97	M	4.04	0.17	0.29[c]	171
8/12/76	0.24	1.93	M	8.04	0.72	0.65	90
8/13/76	0.24	1.93	M	8.04	0.49	0.41	84
8/24/75	0.38	4.00	M	10.53	0.57	0.46	81
8/30/76	0.36	4.56	M	12.00	0.74	0.65	88

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[a] initial values for static experiments established at 0540 EDT and values that would have existed at 1800 EDT in ramp injected experiments if no reaction occurred.

[b] P, propylene; B/P, 60% n-butane-40% propylene by carbon; M, synthetic urban mixture of acetylene, paraffins, and olefins.

[c] NO injection rate for ramped side lower than required to give final NO_x value

The NO_x and HC profiles in these runs are quite different from their static counterparts, not converging until near the end of the run. This convergence implies approximately the same total mass reacted over the same time period.

In another experiment, a highly simplified urban condition was simulated. It was assumed that an air parcel moved along a trajectory over a uniform emissions surface from 0600 to 1200 EDT. At 1200 EDT the parcel left the emissions surface. During its movement over the surface, from 0900 to 1200 EDT the mixing height doubled in a linear manner. Therefore, in the absence of reaction, the concentration of precursors in the air parcel would increase linearly from 0600 to 0900, and then the concentration (mass/volume) would remain constant while an additional three hours of emissions was added to a volume that was doubling in three hours.

This run was compared to a static run which started with the same mass as would be present, in the absence of reaction, at the end of the dynamic run (and also at 0900 EDT). The run was accomplished by ramp injecting NO and HC into a static chamber from 0600 to 0900 EDT, and then diluting the chamber by 50% while continuing to inject NO and HC at a rate equal to the mass lost by dilution assuming no reaction. The results are shown in Figure 6-9. Except for O_3 at the very end of the run and the ramp NO and HC injection, there is

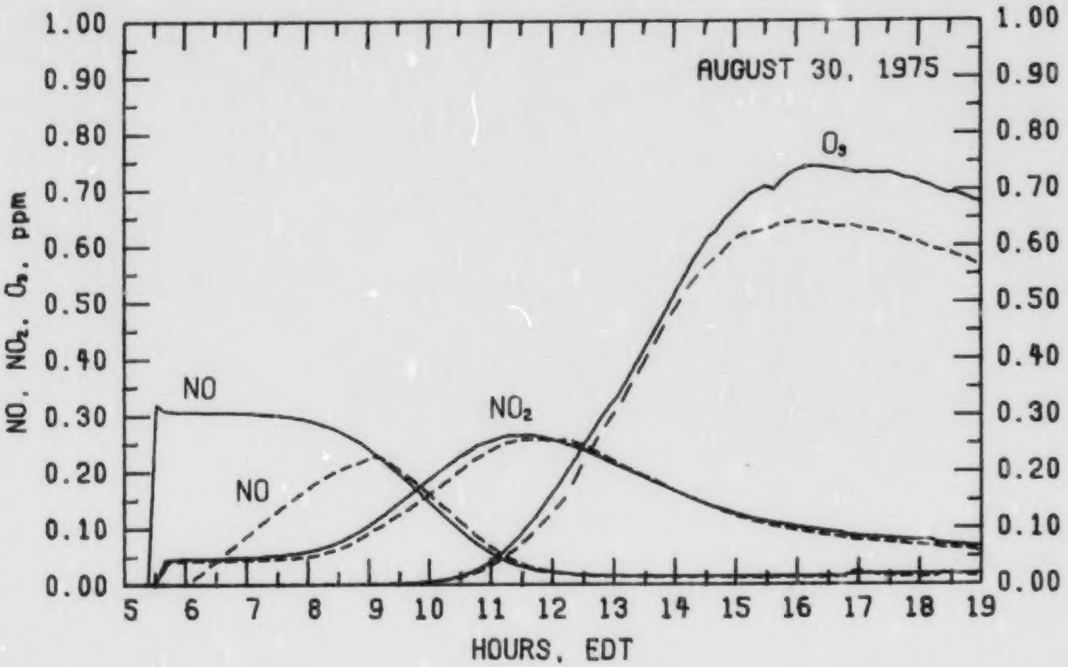

Figure 6. Static (—) and Ramp injection (0600-0900) with 50% dilution (0900-1200) and continued ramp injection (0900-1200) at rate equal to mass removal by dilution if no reaction (--). Initial conditions in static side: NO, 0.31 ppm; NO_2, 0.05 ppm; urban hydrocarbon mix, 4.56 ppmC. An initial condition of 0.05 ppm NO was established in ramp side (--). NO and six injected in (--) so as to achieve same condition at 0900.

almost no difference in the profiles.

Conditions were well matched at 0900, and n-pentane, the least reactive paraffin in the system, is almost constant from 0900 to 1200 EDT. These dynamic runs suggest that it is the total mass emitted into the system divided by the total mixing volume of the system that determined the O_3 produced. These experiments all had a constant HC-to-NO_x ratio for the injected material. Experiments are currently underway to test the effects of varying the HC-to-NO_x ratio around an average value to determine the degree to which the response of the system is dependent upon how the mass is injected.

Assuming that, within limits, the maximum O_3 produced is dependent upon the total mass of the precursor emitted divided by the total mixing volume at the time the maximum occurs, and that this O_3 is 90% of that obtained from the equivalent concentration (mass/volume) irradiated in a static chamber with the same light-intensity and relative speed, then static O_3 isopleths can be used to estimate control requirements.

The intersection of an O_3 isopleth, 1.11 times the highest observed O_3, and a HC-to-NO_x ratio line, obtained by dividing the sum of the total HC emis-

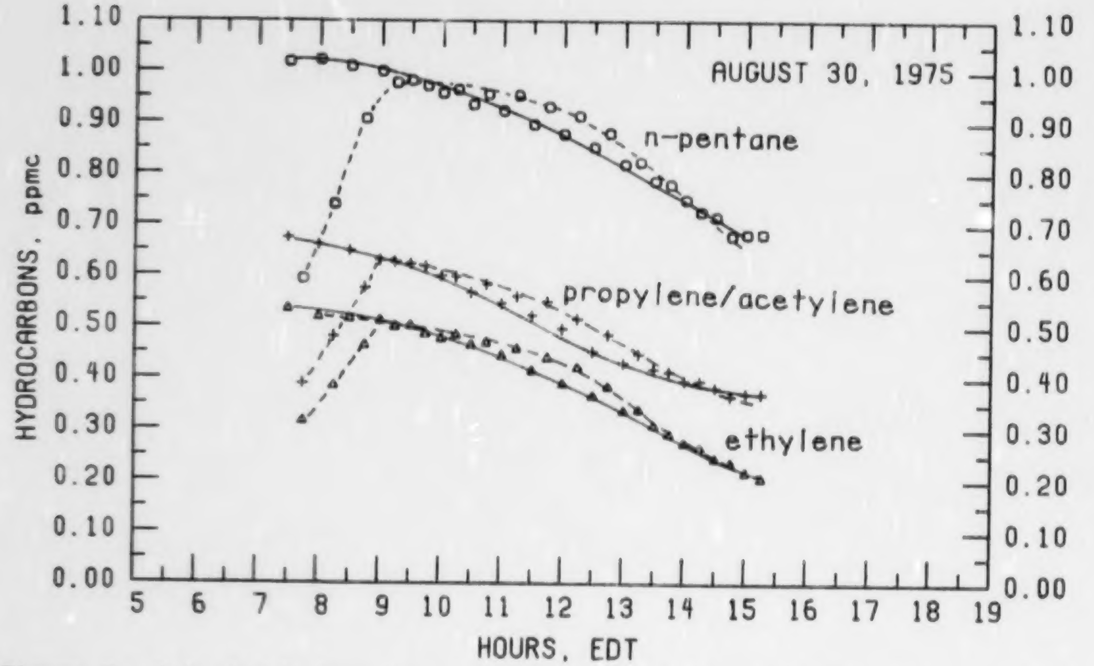

Figure 7. Selected hydrocarbon compounds in urban hydrocarbon mix for Static (—) and ramp injection (--) dual run in UNC outdoor smog chamber.

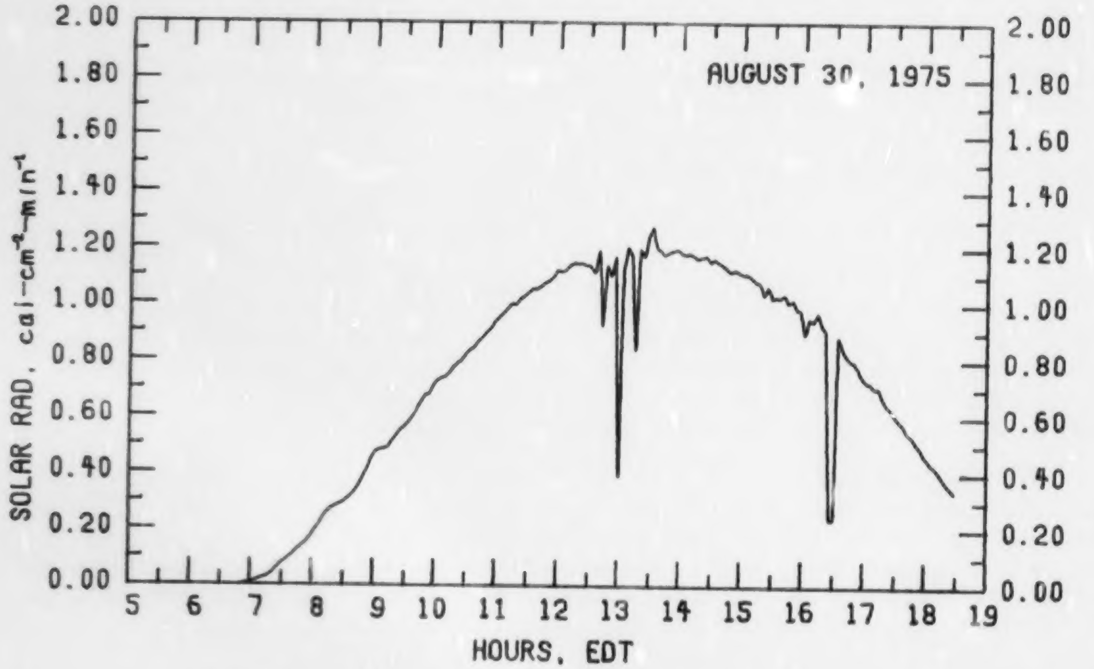

Figure 8. Solar radiation for August 30, 1975.

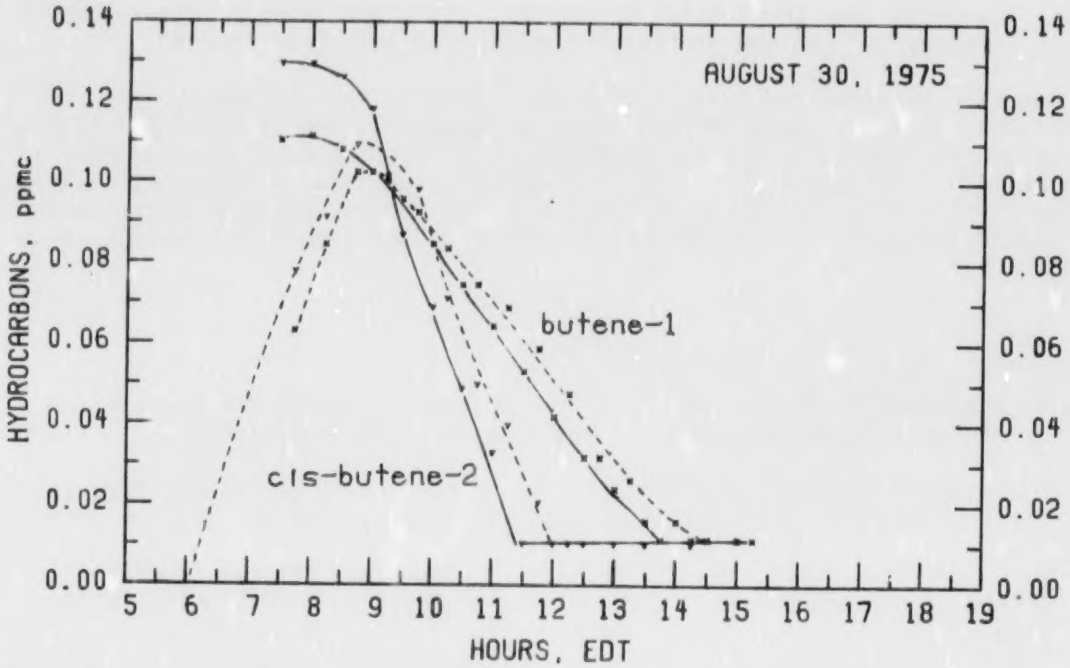

Figure 9. Selected hydrocarbon compounds in urban hydrocarbon mix for static (—) and ramp injection (--) dual run in UNC outdoor smog chamber.

sions by the sum of the total NO_x emissions over the trajectory of the air parcel for the day, would define the static initial HC concentration and initial NO_x concentration which would give rise to the observed O_3. Note that these would also be the concentrations that would be observed in the air parced at the time of O_3 maximum if no reaction had occurred. These precursor concentration and emissions are related by a mixing volume, which would be a critical mixing volume for this trajectory because it gave rise to the highest O_3. Emissions can be reduced such that, if this critical mixing volume occurred again, ambient concentrations of precursors would not become large enough to cause the O_3 formed to exceed a given value. This is essentially the technique proposed by Dimitriades, with the exception that the HC-to-NO_x ratio line is obtained by considering the total daily emissions.

CONCLUSIONS

Based on experiments performed in the UNC outdoor smog chamber, static O_3-HC-NO_x relationships have a good potential for estimating O_3 yields in the "real atmosphere" if the factors discussed are taken into account. Specifically, a method must consider:

- duration and maximum intensity values for diurnal light intensity and for the season in which control is desired,
- the appropriate relative speed for the photochemical system, which

depends upon the initial NO_2-to-NO_x ratio, the rates of heterogeneous processes, and the presence of photoacceptors other than NO_2.

We have hypothesized that, within the limits of typical atmospheric conditions, the total mass emitted into the system divided by the total mixing volume at the time of O_3 maximum determines the O_3 produced. If experimental work verifies this hypothesis, then the initial conditions of the statically-derived isopleths can be directly related to the concentration of precursors that would have been in the ambient air parcel at the time of O_3 maximum if no reaction had occurred.

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THE USE OF TRAJECTORY ANALYSIS FOR DETERMINING EMPIRICAL RELATIONSHIPS AMONG AMBIENT OZONE LEVELS AND METEOROLOGICAL AND EMISSIONS VARIABLES

E. L. Meyer, Jr., W. P. Freas, III, J. E. Summerhays
and P. L. Youngblood*

ABSTRACT

Low-level upper air trajectories were computed for parcels of air arriving at three urban and three rural sites at 1800 GMT during July and August 1974. The most recent 72 hours of each trajectory were divided into time segments varying in length from three to twelve hours. Each segment was characterized by the existing meteorological variables and the total hydrocarbon and nitrogen oxide emissions encountered from manmade sources. Ground level ozone concentrations at the end points of the trajectories were related statistically to emission and meteorological variables encountered in each trajectory segment. Contrast of urban and rural sites tends to substantiate the importance of local precursor emissions. Nevertheless, observed levels of ozone seemed more highly correlated with meteorological variables, particularly temperature. The prime utility of the method reported herein is seen as qualitatively substantiating relationships which have been hypothesized, on a physical basis, between ozone and precursor emissions, and between ozone and meteorological variables.

INTRODUCTION

Until a few years ago, the photochemical oxidant problem was believed to be one which centered primarily in the vicinity of a few urban areas. Control strategies to reduce the level and frequency of harmful concentrations of photochemical oxidant were designed primarily on this basis. During the past several years, however, a number of observations in non-urban areas have indicated that violations of the primary National Ambient Air Quality Standard (NAAQS) for photochemical oxidant are far more ubiquitous (1-5). This new information is likely to have far-reaching implications on the evolution of oxidant control strategies, although as yet, specific implications are difficult to identify. At least two questions need to be addressed before the full implications of high observed levels of photochemical oxidant (measured as ozone) in rural areas can be assessed. First, how important a determinant of ambient ozone are locally generated precursors, as opposed to precursors and

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ozone which are advected into an urban area? Second, what is the relative importance of different meteorological variables at different specified time segments along an air parcel's trajectory?

PROCEDURE

Six monitoring sites were chosen to serve as trajectory end points. It is believed that the selected sites represent situations in which transport of precursors and ozone, as opposed to local precursor emissions, is likely to be important to differing degrees. In the ensuing analysis, local emissions are considered to be precursors emitted within 3-6 hours of an hourly ozone concentration observed at the monitoring site. Thus, locally generated emissions were frequently confined to the county containing the monitoring site and perhaps one or two upwind counties as well, depending on the wind speed. A single monitoring site was chosen at each of the following locations.

- Indianapolis (thought to represent a city with moderate non-methane hydrocarbon (NMHC) and nitrogen oxides (NO_x) emissions, dominated by mobile sources and having relatively low upwind emissions outside of the county).
- Houston (thought to represent a city with very large NMHC and NO_x emissions, dominated by stationary sources and having relatively low upwind emissions outside the county).
- Boston (thought to represent a city with high NMHC and NO_x emissions, dominated by mobile sources and frequently having significant upwind emissions outside of the county).
- Poynette, Wisconsin (thought to represent a location having locally low emissions with only moderate upwind emissions outside of the county).
- McConnelsville, Ohio (thought to represent a location having locally low emissions with potentially high emissions occurring upwind outside of the county).
- Dubois, Pennsylvania (thought to represent a location having locally low emissions with potentially high emissions occurring upwind outside of the county).

The selected sites in the three urban locations (Indinapolis, Houston, Boston) are all in the predominantly downwind direction from each of the cities (i.e., the 71st Street & Takoma, Aldine, and Medford sites, respectively).

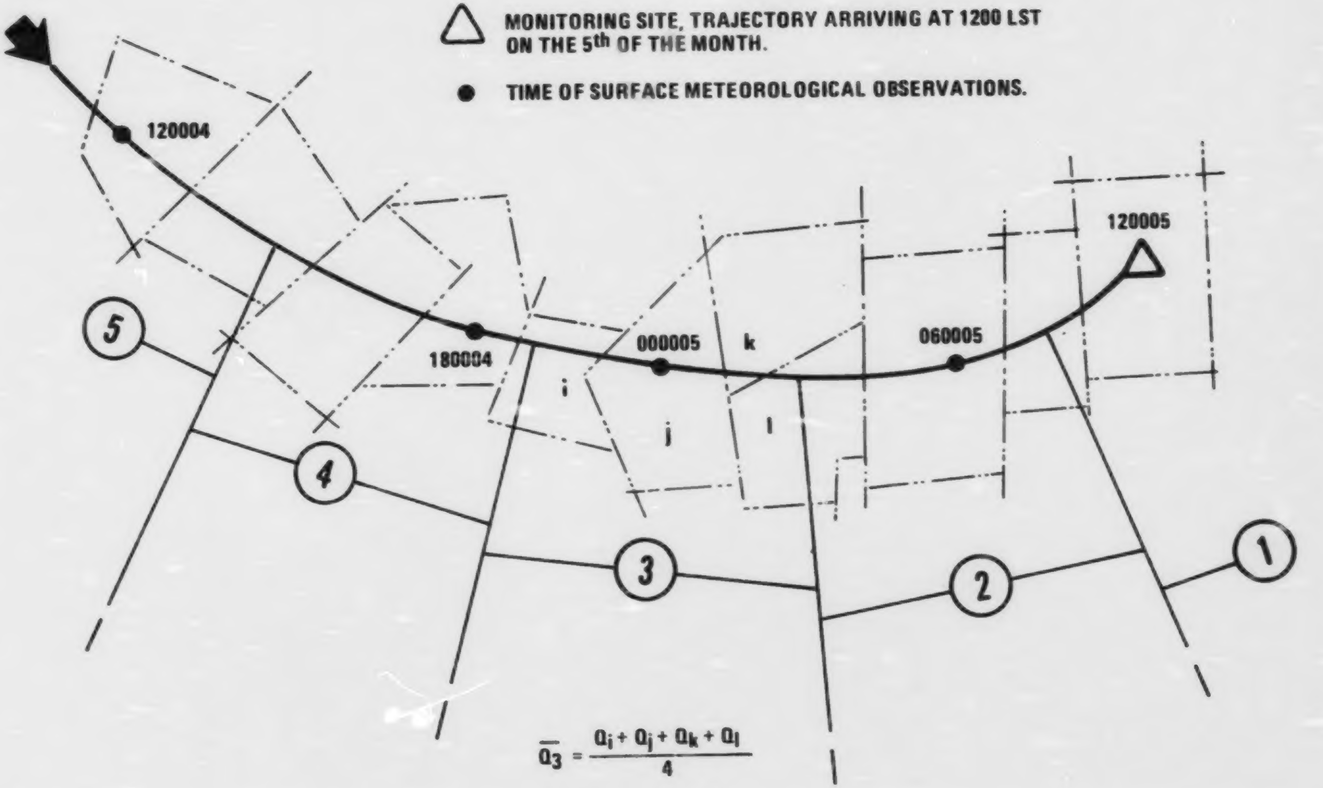
Once trajectory end points were selected, upper air trajectories were estimated using a model developed by Heffter and Taylor (6). Each derived trajectory traces the movement of a hypothetical parcel of air which arrives at a specified monitoring site on a specified day at 1800Z (1400 EDT, 1300 CDT). The movement depicted by the trajectories represents the average wind velocity in a layer of air 300-2000 meters above terrain. One trajectory was plotted for each day between July 1, 1974 and August 31, 1974 at each of the sites for a total of 372 trajectories.

Each trajectory was next superimposed on national maps depicting total hydrocarbon (THC) and NO_x emission density ($t/y-mi^2$) arising from anthropogenic activities in each county in the United States. County emission densities were estimated using the National Emission Data System (NEDS) maintained in the Office of Air Quality Planning and Standards. Trajectories were then segmented as indicated in Table 1. Mean THC and NO_x emission densities were estimated for each segment by averaging the emission densities of the various counties traversed by that segment of the trajectory, as picutured in Figure 1. In segment 1, additional consideration is made of emissions carried past the monitoring site by the surface wind. This latter estimate was made by plotting the location of the monitoring site and point sources of THC and NO_x on a county map and suballocating county area source emissions according to population distribution within the county. By assuming that the observed surface wind velocity at 1800 GMT prevailed during the previous hour, it was possible to estimate the mean THC and NO_x emissions encountered by the surface wind. The mean emissions encountered by the surface winds during the last hour were averaged along with the mean emission density encountered along one segment of the upper air trajectory (calculated as described previously for other segments) to obtain an estimate of mean emissions during the last 3 hours prior to arrival of the air parcel at the monitoring site. Thus, emissions encountered within 3 hours of the ozone concentration observed at each trajectory's end point reflect the impact of both surface and transport layer winds.

TABLE 1. TRAJECTORY SEGMENTS

Segment Number	Time Range (EDT) for Emissions	Time Intervals (hours)	Time of Surface Meteorological Observations (EDT)	Hours Prior to (O_3) Observation
1	1100-1400	3	1400	00
2	0500-1100	6	0800	06
3	2300-0500	6	0200	12
4	1700-2300	6	2000	18
5	1100-1700	6	1400	24
6	0500-1100	6	0800	30
7	2000-0500	9	0200	36
8	0800-2000	12	1400	48
9	2000-0800	12	0200	60
10	0800-2000	12	1400	72

As a result of the procedure described in the previous paragraph, the THC and NO_x emissions encountered in each segment were computed by determining the



MONITORING SITE, TRAJECTORY ARRIVING AT 1200 LST ON THE 5th OF THE MONTH.
TIME OF SURFACE METEOROLOGICAL OBSERVATIONS.
120004
180004
000005
060005
120005
i
j
k
l
1
2
3
4
5

$$\overline{Q_3} = \frac{Q_i + Q_j + Q_k + Q_l}{4}$$

WHERE $Q = t/y \cdot mi^2$

Figure 1. Trajectory notation.

mean of the annual emission values of the counties transversed. However, one would expect seasonal and diurnal variations as well as variations by day of week to occur about this mean. Subsequent review indicated that seasonal changes may be relatively small (8). Therefore, only diurnal and day-of-week emission patterns were superimposed on the estimated annual average emission rate calculated for each segment. The diurnal and weekly emission patterns assumed are based on data available for St. Louis (9, 10).

Surface meteorological observations recorded at 68 National Weather Service, Air Force, and Navy weather stations across the eastern two-thirds of the United States were used to derive appropriate values for the meteorological variables considered in each segment of each trajectory. Observations at the weather station nearest to each segment's mid-point were used as an estimate of conditions along the segment (see Figure 1).

In addition to the meteorological data directly available from weather observations, solar radiation, atmospheric stability conditions, and absolute humidity estimates were derived for each segment. Solar intensity was derived as a function of the time of the day, day of the year, latitude and longitude, and cloud cover. The Pasquill-Gifford stability class was determined from the derived estimate of solar radiation (or cloud cover observations at night) and surface wind speed, using the method described in Turner's Workbook (9, 11). Table 2 summarizes the meteorological parameters available or derived for each segment of every trajectory.

TABLE 2. METEOROLOGICAL PARAMETERS CHARACTERIZING
EACH SEGMENT OF EVERY TRAJECTORY

Trajectory	Segment	Meteorological Characteristics
i	j	Cloud Cover (CC)
		Ceiling (CL)
		Visibility (V)
		Surface Temperature (T)
		Relative Humidity (RH)
		Surface Wind Speed (SP)
		Surface Wind Direction (D)
		Precipitation (PR)
		Transport-layer Wind Speed (W)*
		Solar Radiation (SR)
		Atmospheric Stability (ST)
		Absolute Humidity (A)

* Average horizontal wind speed in a layer 300-2000 meters above terrain.

Correlation coefficients were calculated between the 1800Z ozone concentration and each of the meteorological and emissions variables from each trajectory segment. Those correlations significant at the 5% level for selected meteorological and emissions variables are shown in Table 3 for individual sites, for urban vs. rural sites, and for all sites combined.

Using the combined data set, correlations between all possible pairs of meteorological and emission variables were determined. Statistically significant correlations are depicted in Table 4. The combined data were also used for a stepwise regression analysis. The stepwise regression procedure was used to identify the set of meteorological and HC and NO_x emissions variables which appeared to be the most important in predicting 1800Z ozone concentrations. The results of the analysis have been summarized in Table 5.

DISCUSSION OF RESULTS

The correlation analyses indicated a substantial degree of variability among the six sites. This variability could be attributed to the location of the individual sites with respect to the distribution of sources of precursors, the relatively small range of certain variables (particularly emission variables) at any one site, and the somewhat smaller data base available for some sites. Therefore, it is probably most informative to group the data by sites to seek out, on a qualitative basis, relationships among ambient levels of ozone, precursor emissions, and meteorological variables. In this vein, it is of interest to compare urban and rural sites in Table 3. The correlation between local precursor emissions and ozone is significant and positive at the urban locations. (It should also be noted from Table 4, however, that there is a high degree of intercorrelation between HC and NO_x emissions during any given time period). In contrast, the rural sites exhibit no apparent relationships between local manmade precursor emissions and ozone. Instead, early morning upwind NO_x emissions, and hydrocarbon emissions on the previous day, appear to be positively correlated with ozone observed at the rural locations. Relationships between ozone and meteorological variables are remarkably similar at the two types of sites. The major difference in meteorology-ozone relationships between urban and rural sites indicated by the correlation analysis is with respect to local transport-layer wind speed (Woo). The relationship between local transport-layer wind speed and ozone appears to be a negative one at the urban sites, whereas no apparent relationship exists at the rural sites. This anomaly with respect to wind speed is not surprising. In urban areas, one would expect a higher wind speed to dilute the nearby relatively dense emissions more rapidly and carry them beyond the monitoring site before optimum conditions for photochemical ozone formation are attained. As with urban sites, the effect of wind speed on ozone levels at rural locations would be expected to vary according to the position of the monitor with respect to emissions. However, at rural sites the distances between the ozone monitor and major sources of precursors is expected to be much more variable than at urban sites. All of the foregoing observations tend to support the contention that ozone levels near urban areas are positively related to precursor emissions in the city and environs.

The results of the stepwise regression analyses of the combined data set are also consistent with what one might expect. Among the variables considered, temperature (Too) appears to be the single most important indicator of

TABLE 3. CORRELATIONS FOR 18007 OZONE CONCENTRATIONS SIGNIFICANT AT THE 5% LEVEL

OZONE SITES	Too	T24	SRoo	SR24	RHoo	Aoo	SToo	PRoo-18	PR24	Woo	W24	HCoo	HC06	HC12	HC18	HC24	HC30	NOXoo	NOX06	NOX12	NOX18	NOX24	NOX30
Urban Sites	.52		.27	.33	-.31	.23	-.28	-.37	-.21	-.26	-.29	.23					.16	.13					.26
Boston	.37		.28			.38		-.27															
Houston	.48		.46		-.54		-.35	-.40		-.37	-.38	.47			.43			.43			.43		.34
Indianapolis	.66	.32	.49	.52	-.56		-.25	-.43	-.36	-.44	-.37	.31	.34					.27					.26
Rural Sites	.54	.31	.33	.30	-.28	.21	-.15	-.21			-.27					.16	.23		.23				
Dubois	.55	.31	.42	.57				-.29	-.30		-.29												
McConnelsville	.60		.14		-.36			-.37		-.25	-.36					.30	.27						
Poynette	.71	.50	.48	.31	-.46	.40					-.37					.31	.32		.51			.28	.28
All Sites	.52	.26	.29	.31	-.30	.20	-.21	-.29	-.18	-.16	-.28	.11					.20						.19

Note: Column headings identify meteorological and emissions variables and the trajectory segment. For example, "Too" is the surface temperature estimated for trajectory segment number 1 (see Table 1).

TABLE 4. CORRELATIONS AMONG SELECTED MET AND EMISSIONS VARIABLES SIGNIFICANT AT THE 5% LEVEL-ALL SITES

	Too	T24	SRoo	SR24	RHoo	Aoo	SToo	PRoo-18	PR24	Woo	W24	HCoo	HC06	HC12	HC18	HC24	HC30	NOXoo	NOX06	NOX12	NOX18	NOX24	NOX30
Too	1.00	.57	.37	.45	-.51	.47	-.19	-.34	-.30			.19						.18					
T24	.57	1.00		.35		.50			-.27	.14		.27		.12				.30		.13			
SRoo	.37		1.00	.41	-.58	-.23	-.38	-.35	-.24	-.11											-.16		
SR24	.45	.35	.41	1.00	-.41		-.20	-.29	-.43							-.11					-.12	-.14	
RHoo	-.51		-.58	-.41	1.00	.50	.25	.44		.15											.12		
Aoo	.47	.50	-.23		.50	1.00						.21						.29					
SToo	-.19		-.38	-.20	-.25		1.00	.18	.12	.41	.18												
PRoo-18	-.34		-.35	-.29	.44		.18	1.00	.28	.19	.12												
PR24	-.30	-.27	-.24	-.43			.12	-.28	1.00														
Woo		.14	-.11			.15	.41	.19		1.00	.40	-.11											-.15
W24							.18	.12		.40	1.00										-.11		-.16
HCoo												1.00	.25					.61	.14		.11		
HC06												.25	1.00	.35	.16	.17	.11	.19	.68	.27	.22		
HC12													.35	1.00	.35	.16	.19		.30	.81	.55	.13	
HC18													.16	.35	1.00	.23	.12		.13	.37	.69	.32	
HC24													.17	.16	.23	1.00	.48		.26	.19	.25	.65	.25
HC30													.11	.19	.12	.48	1.00		.15	.11	.13	.20	.56
NOXoo												.61	.19					1.00	.13				
NOX06												.14	.68	.30	.13	.26	.15	.13	1.00	.35	.19	.12	
NOX12													.27	.81	.37	.19	.11		.35	1.00	.57	.14	
NOX18												.11	.22	.55	.69	.25	.13		.19	.57	1.00	.31	
NOX24														.13	.32	.65	.20		.12	.14	.31	1.00	.13
NOX30																.25	.56					.13	1.00

TABLE 5. STEPWISE REGRESSION RESULTS - ALL SITES

Number In Model	R-Square	Variables in Model							
1	.2658	Too							
2	.3369	Too	W24						
3	.3619	Too	W24	HC30					
4	.3794	Too	SR06	W24	Hc30				
5	.3851	Too	NO_x	SR06	W24	HC30			
6	.3914	Too	HCoo	NOXoo	SR06	W24	HC30		
7	.3966	Too	HOoo	NOXoo	SR06	NOX24	W24	HC30	
8	.4016	Too	HCoo	NOXoo	SR06	NOX24	Woo	W24	HC30
9	.3966	Too	HCoo	NOXoo	SR06	NOX24	W24	HC30	
Final Coefficient Signs		(+)	(+)	(-)	(+)	(+)	(-)	(+)	

The variables in the above model have all been deemed significant at the .10 significance level

Note: The modified forward selection technique, available in the Statistical Analysis System (SAS)(7), was used in deriving significant variables and their signs.

ozone. This is consistent with other observations (12, 13), and probably reflects the fairly high intercorrelation of temperature with solar radiation (SRoo) (Table 4) as well as faster reaction rates at higher temperatures. Wind speed (transport-layer) (W24) on the previous day is seen as the second most important variable and appears to be inversely related to ozone levels. The inverse relationship may reflect the tendency for higher concentrations to occur during multiday stagnation episodes and may further reflect the importance of upwind emissions at rural sites. Indeed, the inclusion of hydrocarbon emissions early on the previous morning (HC30) and the previous day's NO_x emissions (NOx24) as significant variables positively affecting ozone levels is further evidence that upwind emissions are important. Other significant variables resulting from the stepwise regression are morning solar radiation (SRoo) and local HC and NO_x emissions (HCoo, and NO_xoo). It is of interest to note that the sign of the coefficient for local NO_x emission is negative. This is in contrast to the positive coefficients for hydrocarbon emissions and for upwind NO_x emissions, perhaps reflecting the fact that NO_x is emitted primarily as nitric oxide (NO), which acts as a scavenger of ozone, before subsequently being oxidized to nitrogen dioxide (NO_2), an ozone precursor.

CONCLUSIONS

- There is considerable variability among individual sites with regard to the correlations between ambient ozone levels and the emission and meteorological variables.
- Generally, ozone levels appear to be more highly correlated with meteorological variables (particularly temperature) than with emission variables.
- Contrasts between rural and urban data suggest that local precursor emissions do play a role in ozone formation and that the relationship between hydrocarbon emissions and ozone levels is a positive one. Coefficients obtained in the stepwise regression analysis suggest that NO_x emissions may initially be inversely related to ozone levels, but the relationship subsequently becomes a positive one. This change in sign is consistent with the role of NO as a scavenger of ozone and the role of NO_2 as an ozone precursor.
- The prime utility of statistical analyses similar to the ones described herein may be to qualitatively support relationships which have been hypothesized on a physical basis. The statistical analysis is limited by the crudeness of the data base (e.g., emissions) and analytical tools (e.g., trajectory model) as well as the peculiarities of individual sites. In the stepwise regression analysis, only about 40% of the variance in afternoon ozone levels is explained by the statistically significant emissions and meteorological variables. Nevertheless, the variables selected as statistically significant and their signs are consistent with current theories concerning the formation and transport of ozone.

ACKNOWLEDGMENTS

The authors would like to acknowledge the efforts of the Simulation Support Section, Source Receptor Analysis Branch, Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards, U. S. EPA. Through the efforts of this group, computer generated emission density maps were made possible. This work would not have been feasible without such maps.

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SESSION 19

OXIDANT-PRECURSOR RELATIONSHIPS AND THEIR INTERPRETATION IN TERMS OF OPTIMUM STRATEGY FOR OXIDANT CONTROL - II

Chairman: E.L. Meyer
Environmental Protection Agency

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REPORT ON OXIDANTS AND THEIR PRECURSORS IN CANADA

L. Shenfeld*

ABSTRACT

Oxidants (ozone) are being measured at several locations across Canada. At present the method of sampling is by the chemiluminescent principle and specifically ozone is being monitored. High concentrations have been most prevalent in Southern Ontario. These have occurred mainly during the summer, with weather favourable for photochemical reactions in the atmosphere. High measurements in remote rural areas indicate evidence of the long distance transport of oxidants as well as that of the precursors, nitrogen oxides and hydrocarbons, which lead to the formation of oxidants. The origin of the pollutants present in Southern Ontario has been on a frequent basis traced to the industrialized areas of the Northeastern United States.

INTRODUCTION

Ozone (O_3) is presently being measured in most of the large cities across Canada by chemiluminescent instruments. The locations of these Cities that are outside of the Province of Ontario are shown in Figure 1. The highest oxidant (ozone) measurements in Canada have been obtained in Southern Ontario where monitoring began in 1969. This area (shown hatch-marked in Figure 1) extends southward to a latitude equivalent to Northern California. The sampling locations recording oxidants (ozone) that are discussed in detail in this report are Windsor, Sarnia, Simcoe, Hamilton, Metropolitan Toronto, Stouffville and Ottawa. The locations of these are shown in Figure 2. The sampling sites are in urban areas, except for Simcoe and Stouffville which are in rural farming areas.

CANADA'S AIR QUALITY OBJECTIVES AND OXIDANT LEVELS

The Canadian air quality objectives are given in Table 1.

The Maximum Desirable Level defines the long-term goal for air quality and provides a basis for anti-degradation policy for the unpolluted parts of Canada and the continuing development for control technology. Maximum Acceptable Levels are intended to provide adequate protection against any

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*Ontario Ministry of Environment, Canada.

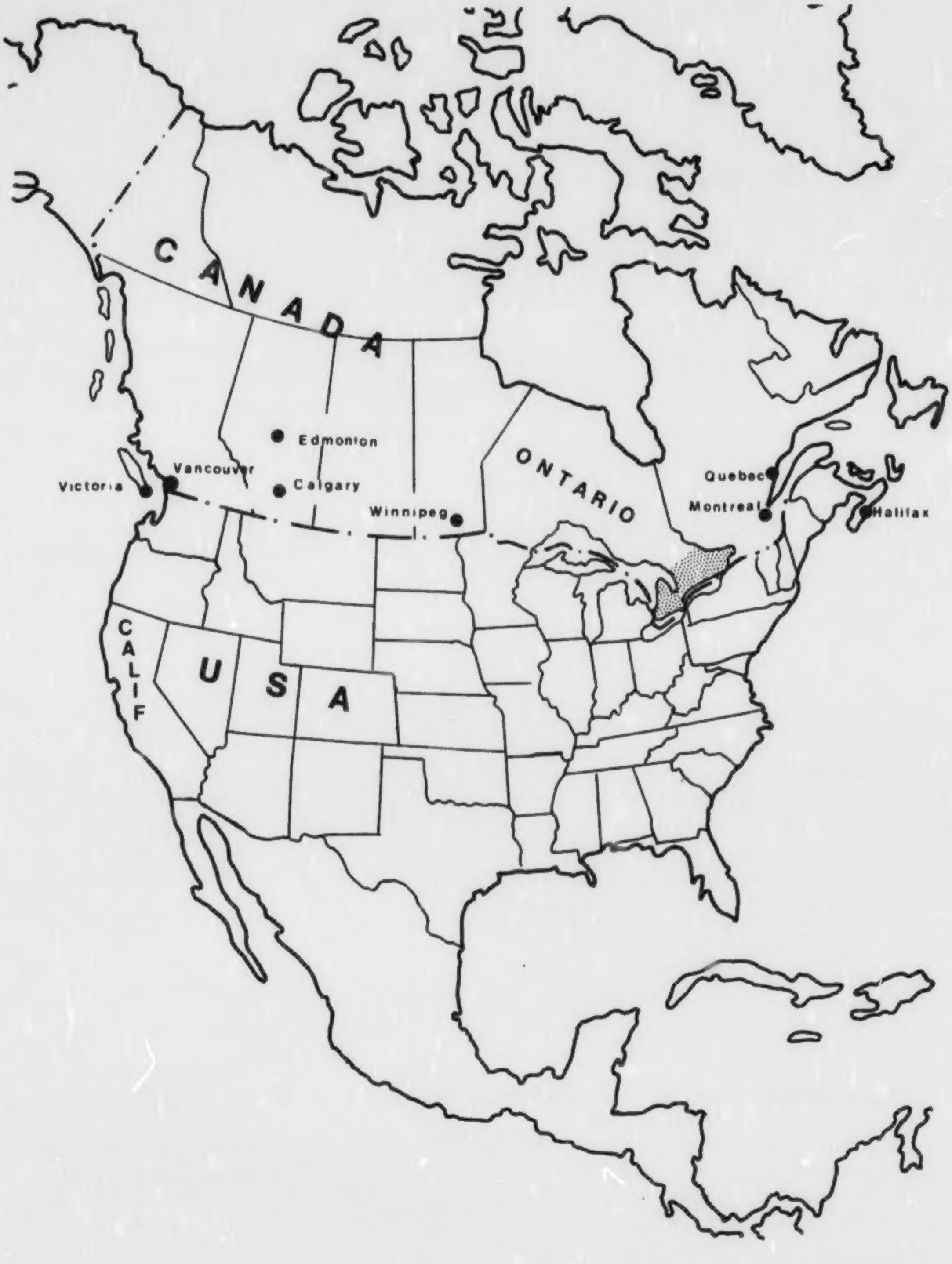

Figure 1. Location map.

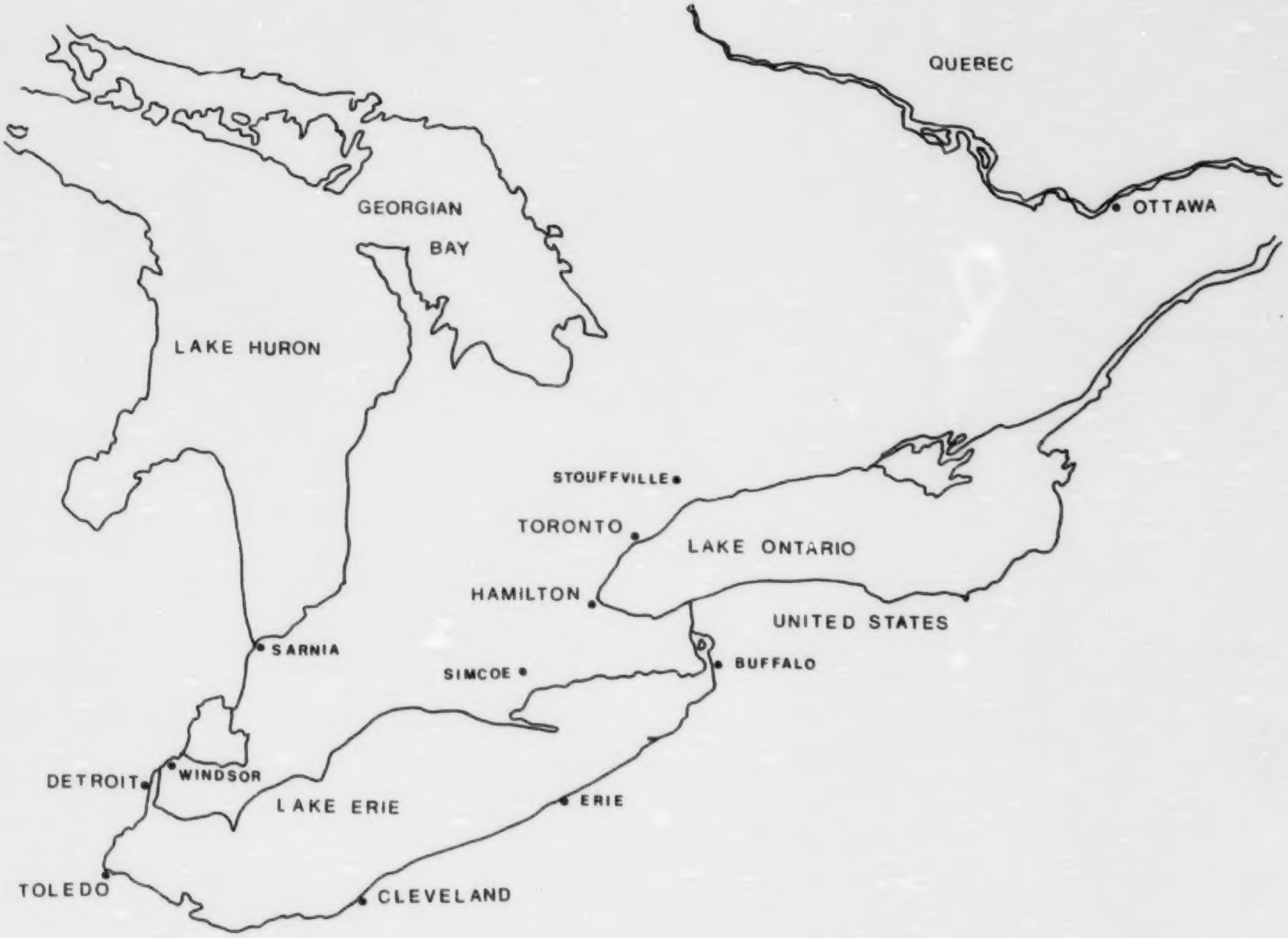

Figure 2. Southern Ontario, Canada. Sampling stations and urban centres.

TABLE 1. CANADIAN AIR QUALITY OBJECTIVES

Pollutant	Averaging Time	Maximum Desirable Levels $\mu g/m^3$	Maximum Desirable Levels ppm	Maximum Acceptable Levels $\mu g/m^3$	Maximum Acceptable Levels ppm	Proposed Max. Tolerable Levels $\mu g/m^3$	Proposed Max. Tolerable Levels ppm
Oxidants	1 hr	100	0.05	160	0.08	300	0.15
	24 hrs	30	0.015	50	0.025	*	*
	1 yr	*	*	30	0.015	*	*
Nitrogen Dioxide	1 yr	*	*	400	0.20	1000	0.50
	24 hrs	*	*	200	0.10	300	0.15
	1 yr	60	0.03	100	0.05	*	*

* Not established

adverse effects of the pollutants. Maximum Tolerable Levels denote concentrations of air pollutants that require abatement without delay so as to avoid further deterioration that could ultimately pose a substantial risk to public health.

No air quality objectives have as yet been set for hydrocarbons (HC).

Levels of oxidants (ozone) are at times exceeding the maximum desirable and maximum acceptable levels at almost all of the sampling locations in Canada, the frequency of exceeding these objectives being greatest in Southern Ontario. At some of the locations the Proposed Maximum Tolerable Objective is exceeded during several hours per year (Table 2.)

TABLE 2. NUMBER OF HOURS OZONE LEVELS EXCEEDED OBJECTIVES

LOCATION	MAXIMUM DESIRABLE 100ug/m^3 (0.05ppm)		MAXIMUM ACCEPTABLE 160ug/m^3 (0.08ppm)		MAXIMUM TOLERABLE 300ug/m^3 (0.15ppm)	
	1974	1975	1974	1975	1974	1975
Windsor	363	482	59	155	0	14
Sarnia	370	618	80	132	0	4
Simcoe	1004	1084	135	141	0	0
Hamilton	396	986	37	317	0	6
Toronto (Central)	619	1175	146	386	1	11
Toronto (Suburban)	325	685	43	181	0	0
Ottawa	*	541	*	85	*	0

* Insufficient data

The maximum concentration of oxidants recorded in Canada was 700 ug/m^3 (0.35 ppm), occurring in August 1971 in a northwest suburb of Metropolitan Toronto. The measurement was of total oxidants obtained with an instrument using a colourmetric method. All monitoring instruments have since been changed to those utilizing the chemiluminescent principle. The highest ozone level measured in Canada by this means was 550 ug/m^3 (0.274 ppm). This level occurred in August of 1975 at Windsor, Ontario.

RELATIONSHIP OF MAXIMUM OZONE LEVELS WITH LEVELS OF HYDROCARBONS AND NITROGEN OXIDES

High levels of ozone at an urban location in Toronto and a rural location, Simcoe, were divided into two ranges for analyses, 0.080-0.099 inclusive and levels equal or greater than 0.10 ppm. Table 3 gives the average levels of total hydrocarbons, nitric oxide NO), nitrogen dioxide (NO_2), and nitrogen oxides (NO_X) during the morning hours 06:00-08:00 EST that the ozone levels occurred in the two ranges.

TABLE 3. RELATIONSHIP OF DAILY MAXIMUM OZONE
WITH HC AND NOX LEVELS FROM 06:00 to 09:00 am

LOCATION	RANGE OF MAXIMUM OZONE ppm	AVG.OZONE LEVEL ppm	AVG. HC ppm	AVG. NO ppm	AVG. NO_2 ppm	AVG. NO_x ppm
TORONTO	0.080-0.099	0.093	2.28	0.04	0.045	0.076
	≥ 0.10	0.117	2.47	0.03	0.048	0.082
SIMCOE	0.080-0.099	0.084	1.95		0.019	
	≥ 0.10	0.106	2.07		0.016	

The data indicates a positive relationship existing between the daily maximum levels of ozone and the average concentration of total hydrocarbons measured from 6 and 9 a.m. There is little if any relationship evident between the maximum ozone and levels of nitrogen oxides. The data indicates that at rural Simcoe location lower levels of hydrocarbons were associated with the maximum ozone than in urban Toronto. This may indicate that the ozone is likely produced elsewhere and transported to the rural location.

AVERAGE DAILY MAXIMUM OZONE LEVELS AND TIME OF OCCURRENCE

The average of the maximum daily ozone concentration and the time that the maximum occurred are given in Table 4.

TABLE 4. AVERAGE DAILY MAXIMUM OZONE LEVELS
AND HOUR OCCURRED E.S.T.

Month	April	May	June	July	Aug.	Sept.
Avg.Max. Conc.ppm	0.037	0.041	0.053	0.064	0.064	0.044
Hour Ending Max.Conc.	1400	1500	1500	1500	1500	1400

The table indicates the maximum ozone concentrations occurring in July and August, with the time of occurrence during the afternoon hour ending at 1400 during April and September and at 1500 Eastern Standard Time (EST) from May and August.

RELATIONSHIP OF OZONE LEVELS AND WEATHER CONDITIONS

An analysis of weather data during days of high ozone levels, (maximum greater than 0.08 ppm) indicate that skies were predominantly sunny during 85% of the days. About 10% of the high ozone days skies were reported cloudy, but these days followed a sunny high maximum ozone day. During these periods the ozone formed during the previous day was not dispersed or reactively reduced by the following day. During the remaining approximate 5% of the days recording high ozone, thunderstorms were reported in the area of the sampling stations. Stratospheric contributions bringing ozone levels above 0.08 ppm is rare. However, on May 17, 1973, concentrations of oxidants in Hamilton reached 0.10 ppm although conditions were not favourable for photochemical reactions. The Polar front was located along a northeast-southwest line through the Appalachians with cyclogenises occurring east of the Lower Great Lakes. The 500 MB map discloses a deep north-south trough over the Great Lakes. This synoptic situation has been described by Reiter(1) as that associated with the folding of the tropopause bringing ozone down from the lower stratosphere to ground. This likely explains the high ozone occurrence on this day. There have been one or two such occurrences of high ozone levels each year that have no other explanation.

The following table provides the percentage of days that the prevailing wind was in the direction indicated on high ozone days:

TABLE 5. RELATIONSHIP OF OZONE LEVELS WITH WIND DIRECTION

DIRECTION	N	NE	E	SE	S	SW	W	NW
% of Days with	2.2	3.3	12.2	5.9	26.9	32.8	14.2	2.2

The above indicates that the favourable wind directions for days of high ozone are from the south and southwest. Winds in this direction occur with high pressure areas located east to southeast of Southern Ontario. Subsidence inversions aloft would be associated with the anticyclone, resulting in limited mixing heights and poor dispersion. Winds from the south and southwest transport air from industrialized areas of the United States into Ontario. Quickert et al.(2) has traced the origin of air-producing high ozone levels in Ottawa back to Ohio.

The high prevalence of days with southwest winds when ozone levels were high at Simcoe would suggest the City of Cleveland, 200 km. away, as the principle source of precursor contaminants (Figure 2). There are no other industrial or traffic sources in the immediate area of the sampling station in the direction from Simcoe. Almost 50% of the days that Stouffville, another rural site, recorded high ozone levels, the winds were in the direction from Toronto. There have been many reports(3,4,5) of high rural levels of ozone in the United States, relating these to emissions from downwind urban centres. The high ozone levels in rural areas are of major importance as documented economic losses to agricultural crops of tobacco, white beans and tomatoes due to oxidants have been reported(6,7,8,9).

The daily average wind speed during high ozone days was generally light, that is, less than 5 metres per second, for 90% of the days recorded. The highest daily average wind speed during which 0.08 ppm was exceeded was 8.8 mps, occurring in Windsor July 13, 1974.

The maximum temperature recorded during days of high ozone were above 25°C during 90% of the days recorded. About 20°C may be considered the lowest daily maximum that high ozone levels could be traced to photochemical reactions. During May 17, 1973, when the high ozone at Hamilton was indicated to have a stratospheric origin, the maximum temperature was only 9°C.

The influence of lake breezes on the development of high ozone levels during the summer in the Toronto area has been noted by Anlauf et al.(10) and Lusis et al.(11). Afternoon levels of ozone as high as 0.16 ppm was measured on Toronto Island, which is just south of Toronto on Lake Ontario, on August 7 and 8, 1974 during a time that a high pressure area was over Southern Ontario. Maximum downtown Toronto levels were 0.047 and 0.076 ppm during the two days. The primary pollutants emitted in the urban industrial shoreline communities are considered to have been carried out over the lake during the night by land breezes. Photochemical reactions took place in the stable air over the lake during the morning and ozone laden air was brought in over the Island by the lake breezes that developed during the day. Lower concentrations measured in the downtown area were considered to be due to the inhibitive action of higher levels of nitric oxide in the area. There is little automobile traffic on Toronto Island. During the period, the levels of ozone in the rural site of Stouffville northeast of Toronto were 0.168 and 0.133 ppm, respectively, similar to that on Toronto Island in the opposite direction from the City.

CONTROL TECHNOLOGY AND LEGISLATION IN CANADA

On a nationwide basis, transportation sources have been attributed to be the major emitters (65%) of nitrogen oxides and hydrocarbons. However, on regional or city-wide emission surveys, large fossil fuel power plants have been shown to be major contributors of nitrogen oxides.

There has been Ontario legislation on the control of hydrocarbons emitted from automobiles sold in the Province as early as in 1968, that is, controlling emissions from 1969 models. In recent years the Canadian Government has assumed jurisdiction and has passed legislation controlling emissions, as indicated in Table 6.

TABLE 6. CANADIAN AUTOMOBILE EMISSION CONTROLS

	Hydrocarbons gms/mi	Nitrogen Oxides gms/mi
1973-74 Vehicles	3.0	3.1
1975-1980 Vehicles	2.0	3.1
Proposed for future	0.41	2.0

With respect to the control of stationary sources, most of the emphasis has been involved in the control of hydrocarbons emitted. Technology to control nitrogen oxide emissions are rarely enforced. Evaporation losses of hydrocarbons in storage tanks are controlled by the use of floating roofs. Other abatement techniques employed by the petroleum and other industries incorporate the use of scrubbers and afterburners.

The success of present technology in the control of emissions of the precursor contaminants to prevent levels of ozone from exceeding 0.08 ppm is doubtful. With the presence of natural sources of hydrocarbons and the long distance transport phenomena, stringent controls on a continental basis would seem necessary.

CONCLUSIONS

High oxidant (ozone) levels measured in Canada have been related principally to photochemical reactions with only 5% of these high levels found to be related to thunderstorms and downward transport of ozone from the stratosphere. Ozone levels over 0.08 ppm are normally associated with sunny skies, afternoon temperatures reaching 25°C, and southerly winds less than 5 mps. The transport of oxidants and their precursors from the industrialized States to the south have caused injuries to agricultural crops in rural Southwestern Ontario. For the prevention of high levels of oxidants and their adverse effects on man, more stringent controls of emissions of both nitrogen oxides and hydrocarbons from stationary sources are likely to be necessary.

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PRECURSOR CONCENTRATION AND OXIDANT FORMATION IN SYDNEY

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ABSTRACT

As its part in the Sydney Oxidant Study, the group at the University of Sydney has commissioned a Mobile Air Analysis Laboratory for measurement of ozone and its precursors: nitrogen oxides and non-methane hydrocarbons. This facility has been used to develop improved calibration procedures for air pollution monitoring instruments and to carry out an extensive programme of field measurements. The field programme has identified suitable sites for the measurement of precursors in the Sydney region, and the mobile laboratory has enabled the development of precursor levels to be observed in air parcels as they are tracked to receptor areas.

Precursor concentrations are lower than expected and not in agreement with predictions of simple dispersion models using current emission inventories. Ozone-precursor relationships are, however, consistent with U.S., Japanese, and European data, although much more work is required to establish a workable correlation for Sydney.

INTRODUCTION

Pollution from photochemical oxidants has been recognized as a serious problem in Sydney since November 1971, when an episode was responsible for considerable damage to petunia seedlings. The Sydney Oxidant Study is a cooperative program of field measurements and research coordinated and funded by the State Pollution Control Commission (SPCC) of New South Wales. The objectives and approach of the study have been outlined by Iverach (1975, 76). A review of existing information on the relationship between oxidants and their hydrocarbon (HC) and nitrogen oxides (NO_x) precursors had shown that there was considerable conflict between correlations developed by the Los Angeles Air Pollution Control District (APCD), the U.S. Environmental Protection Agency, (EPA), the Japanese Environment Agency, and smog chamber researchers. There was thus a great need to develop data for Sydney so that control programs would have a realistic and relevant basis. Briefly, the roles of the various groups in the Study are as follows: University of Sydney, trajectory measurements; Macquarie University, meteorology; CSIRO Division of Process Technology, HC "finger-printing" and smog chamber research; and SPCC, fixed site monitoring and airborne measurements. At Sydney University we are also engaged in numerical modelling of photochemical smog formation (Allen and Bilger, 1976) under a project sponsored by the Australian Research Grants Committee. Funding of the Sydney Oxidant Study began in September 1974 and is being continued until September of 1977 at least. It is believed that the interaction on a continuing basis of these diverse groups is a very important ingredient in the success of the Study.

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At the commencement of the Study, the only monitoring data being obtained were from three fixed-site ozone (O_3) monitors operated by the SPCC, there being almost no reliable information on the precursor NO_X and non methane hydrocarbon (NMHC) (Iverach and Bilger, 1975). A preliminary study of high oxidant days (Hawke and Iverach, 1974) showed the influence of the land and sea breezes during periods of general synoptic stagnation and implicated three main source areas: an inland industrial source around Silverwater; the central business district (C.B.D.) and the industrial region just to the south of it; and a coastal industrial source at Kurnell near the mouth of Botany Bay (Figure 1). There was thus a great need to establish precursor concentrations, correlate their occurrence with known emission sources, and follow the development of the polluted air masses as they pass over the region under prevailing meteorological conditions. The identification of suitable fixed monitoring sites for both precursors and oxidants would be a further result of this work. These then were the first objectives of mobile monitoring project undertaken by the Sydney University group, and they have in large part been achieved. Work is now aimed at quantifying the relationship between emissions and precursor concentrations, correlating the downwind oxidant concentrations with morning precursor concentrations, and validating and developing a numerical trajectory model. It is believed that the continuing iterative interaction between field measurement and modelling sharpens both experimental and analytical techniques and yields new insights into the problem, since "unexplained" factors of 4 and 2 and 1.5 between observations

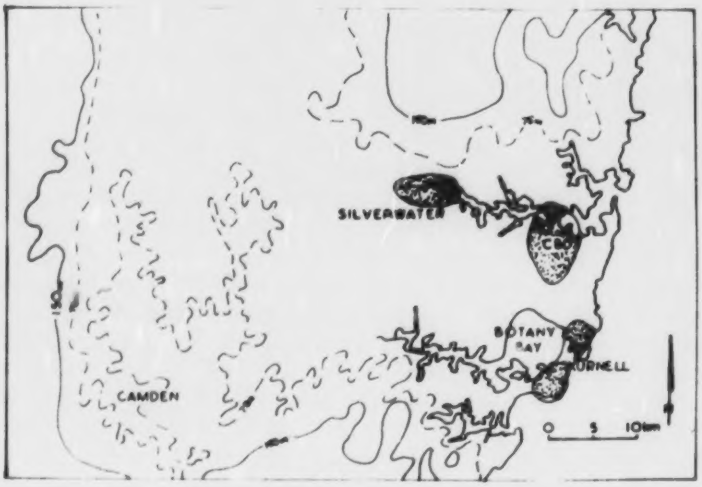

Figure 1. Sydney location map.

and predictions must be investigated. Here we report on the preliminary data obtained and the first round of iteration with the modelling. Earlier reports may be found in Allen and Iverach (1976), Allen (1976), and Allen and Bilger (1976). Full details of the data are summarized in bimonthly and annual reports to the SPCC (Post et al., 1976). It is hoped that the data will attract other modellers and interpreters.

A considerable effort has gone into validation of the calibration techniques used with the ozone, nitrogen oxides and hydrocarbons instruments used in the Sydney University Mobile Air Analysis Laboratory. This work is described in the next section and it gives considerable support to the ozone and NO_X field observations. Problems associated with suitable mobile monitoring sites free from local sources are also discussed in that section as are current uncertainties inherent in continuous Flame Ionization Detector (FID) analyses of ambient hydrocarbon concentration.

Non-methane hydrocarbon and NO_X concentrations measured during the summer oxidant season are considerably lower than those reported for winter conditions by Allen (1975). These observations, however, are in general agreement with those projected from emission inventories by Iverach et al. (1976) but the relationship between ambient levels and upwind sources of different types is not straightforward. These results and the general features of the trajectory measurements are reported in the Results section together with a discussion of attempts to quantitatively relate measured precursor concentrations to emissions. In the last section oxidant-precursor relationships are examined.

INSTRUMENTATION, CALIBRATION, AND PROCEDURES

The Sydney University Mobile Air Analysis Laboratory used in this study has a heat-insulated body shell mounted on a small truck chassis (Bedford Elf 2000cc). It has a 5kVA 240V 50Hz electrical power generator to keep the instruments operating while mobile and a small air cooling unit to remove heat dissipated by the instruments. Sampling is via an all teflon sampling system with an inlet 4 m above the ground. Residence times in the sampling lines are less than two seconds. A full description of the laboratory may be found in Allen (1976).

An MSA model 11-2 dual FID is used to obtain total hydrocarbon and methane data. This instrument is calibrated using NATA certified span gas mixtures supplied by the Commonwealth Industrial Gases Limited (CIG). Zero span gas is generated by the instrument itself by passing the sample stream through a catalyst bed containing Hopcalite at 375°C. A gas mixture of 14.5 ppm methane was used to span both the total hydrocarbon and methane burners and a mixture containing 6.0 ppm methane and 2.5 ppm propane in air was used to determine the sensitivity of the total hydrocarbons burner to hydrocarbons other than methane. High purity hydrogen is used as the fuel and it has been found that the relative molar response (RMR) (Schoefield, 1974; Blades, 1973; David, 1974) obtained for propane could be made to vary between 1.05 and 3.24. Relative molar response factors are a function of burner configuration and fuel. Sample, and combustion air flow rates and the performance of this instrument with respect to its total hydrocarbons function is still under examination. Throughout this period, however, the instrument functioned under conditions which gave a propane RMR of approximately 2.2. All hydrocarbon data were obtained with the instrument operating in this manner. No correction has been applied for non-theoretical RMR behaviour.

Ambient ozone concentrations are determined using a Norian model NCM-100 chemiluminescent analyser. This instrument is calibrated against ozone mixtures generated by a Penray ultraviolet (UV) lamp incorporated in a flow dilution system. The absolute ozone generation rate of this lamp is determined at each calibration by either gas phase titration (GPT) or the neutral buffered potassium iodide (NBKI) procedure. Both analytical methods were consistent to within ten percent (1.56 (±0.06;90%) x 10^{-7} moles O_3 min^{-1} by NBKI, and 1.46 (±0.09;90%) x 10^{-7} moles O_3 min^{-1} by GPT). Post (1976) gives details of these two methods. An untraviolet absorption system is being developed to give a further method of absolute calibration.

Nitric oxide (NO) and total nitrogen oxides are determined using a Monitor Labs model 8440 chemiluminescent analyser. This instrument is calibrated using a flow dilution system together with NATA certified gas mixtures containing 41 ppm and 185 ppm nitric oxide in nitrogen. Calibrations were performed within the range 4 to 400 pphm and instrument grade air (CIG) was used as the diluent. Many interlaboratory comparisons have been performed between the University of Sydney and SPCC. Both groups, using various combinations of dilution systems and span gas mixture cylinders, have generated diluted mixtures which gave interlaboratory agreement to within ten percent. Instrument zero settings have been determined by switching off the ozone generator within the instrument, thereby simulating a zero NO_X condition. This "zero ozone" method is thought to be unsatisfactory and a considerable effort was made to obtain a true zero NO_X sample to get an independent measure of this zero setting. Ascarite (reg. T.M.) was found to be very effective in scrubbing NO and nitrogen dioxide (NO_2) from spiked air streams and was used to manufacture "zero NO_X" from ambient air. This material gives a reading of + 0.3 pphm on the NO channel of an instrument zeroed by the "zero ozone" method. The zero NO_2 signal has been found to vary between - 0.5 and + 0.2 pphm, but since this signal is the result of the subtraction of the NO signal from the total NO_X signal, and is consequently dependent upon the sensitivity of both the NO and NO_X channels, its value from day to day is variable and its absolute value uncertain. Tests using activated charcoal to scrub ozonized instrument grade air have given similar results.

In Figure 2 the quantity $[O_3][NO]/[NO_2]$ is shown as a function of the time of day for March 19, 1976. The smooth curve presented on this plot is the clear sky theoretical $[O_3][NO]/[NO_2]$ -vs- time relationship derived from the solar zenith angle for Sydney in mid-March (calculated from the Nautical Almanac (1976)), the rate constant data of Jones and Bayes (1972) for the reaction $NO_2 + h\nu \rightarrow O_3 + NO$, and the rate constant data of Schofield (1976) for the reaction $NO + O_3 \rightarrow NO_2 + O_2$ corrected for the temperature prevailing at the specified time of day. The relationships used in these calculations are otherwise the same as used by Calvert (1976).

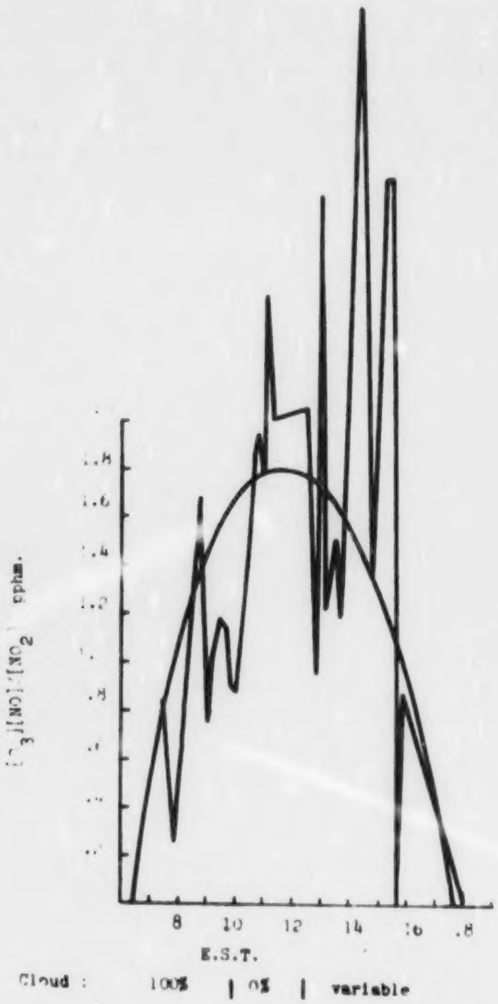

Figure 2. Experiment ratio $[O_3][NO]/[NO_2]$ for March 19, 1976.

The $[O_3][NO]/[NO_2]$ values calculated from the experimental data for this and other days fall around the theoretical relationship and follow the predicted trend throughout the day. The scatter in the experimental data is similar to that obtained by Eschenroeder and Martinez (1970), Stedman and Jackson (1975), Calvert (1976) and in this instance it can be attributed, in part, to the lack of instantaneous O_3, NO, and NO_2 measurements. The data points in these figures were calculated from 3 minute averages which have been corrected for the zero offsets. The $[O_3][NO]/[NO_2]$ ratios calculated with uncorrected NO_x data show no consistency and this supports the view that the zero settings obtained by the "zero O_3" method are incorrect. There is thus considerable support for the accuracy of the corrected NO_x and O_3 data and their interpretation can be attempted with confidence.

Wind speed and direction are measured using small buoyant balloons that are ballasted to give a rate of rise of 1 m/s. The balloon is followed from its release point and the time and horizontal distance travelled (usually about 50 m) is measured to give the wind velocity. The heading after 100 s of flight gives the mean wind direction. The height of low level inversions can be estimated from the time of rise to points where a sudden deviation in drift direction occurs. Air temperature and relative humidity are measured using a hand-held whirling hygrometer outside the laboratory.

On account of the possibility of undispersed local emissions giving values which are not representative of the area or the air parcel being tracked, the measurements were made at sites where these effects were considered to be minimal. The usual sites chosen have been near large areas of parkland with few trees and with the laboratory downwind of the open area. Golf courses, bowling clubs, and sports areas have been found to be ideal for this purpose. Usually mains power was obtained for operating the instruments, but when measurements had to be made with the generator on, the exhaust was directed downwind to avoid contamination of the ambient sample.

"Oxidant Days" are days of predicted stagnant meteorological conditions with all groups called into the field by the coordinator. Measurements are made with the mobile laboratory on Oxidant Days and on many other days when rain or high winds had not been forecast. At other times the van is garaged in the Heat Laboratory in the Department of Mechanical Engineering at the University of Sydney and monitoring is continued from a sample point located above the roof of the building. Mobile measurement strategies included survey work aimed at determining precursor sources, concentrations and suitable sampling sites, and trajectory measurements aimed at tracking air masses from source to receptor areas.

Trajectory measurements have been made on days when the wind is light and high oxidant formation expected. The usual practice has been for high morning concentrations to be located near a known source area and then followed when the winds increased. The trajectory is predicted from the wind speed and direction in the lowest one-hundred metres of the atmosphere measured at each successive site. The mobile laboratory is shifted downwind by the distance the air would move if it continued with the measured velocity. Allowance is made for the monitoring period and time to travel between points on the trajectory. It has been found that this practice has to be modified when travelling in the sea-breeze front. Otherwise one gets ahead of the front. Starting points have been at positions downwind South and East of the C.B.D. and East of the inland industrial source at Silverwater. From the C.B.D. trajectories were followed inland with the sea breeze.

RESULTS

The observations given here are taken from measurements made from October 1975 to April 1976. In this period the calibration of the ozone and oxides of nitrogen monitoring instruments is considered to be accurate to within ten percent both from month to month and in absolute terms. A zero correction of 0.3 pphm has been subtracted from NO concentrations according to the findings above. Hydrocarbon calibration is reported in a consistent way as ppm C (as methane), although no allowance is made for correction for the relative molar response for hydrocarbon components of the ambient mixture.

The distribution of measured half-hour average concentrations of NMHC and NO_X for the morning period 0600 - 0900 at the University of Sydney and other sites is given in Figure 3. These data include measurements on days when either field measurements were made, NMHC exceeded 0.5 ppm, maximum O_3 exceeded 5.0 pphm, or NO_X exceeded 5.0 pphm. For high concentration of NMHC and NO_X, the NMHC-to-NO_X ratios vary between 4 and 12 (ppm C/ppm). It was considered that the NMHC/NO_X ratio would give an indication of the source of precursors, since Australian automobiles tested over the U.S. Federal Driving cycle give emissions approximately in the ratio 5, industrial combustion gives a ratio much lower than this, and refinery emissions, including evaporation, are much higher, being greater than 10 ppm C/ppm. The ambient levels however, are a mixture of emissions from many sources and it has not yet proved possible to isolate predominantly automobile emission from other sources using the NMHC/NO_X ratio. Because of the mixing of the emissions, the ambient levels are compared with predicted emission levels using inventory data.

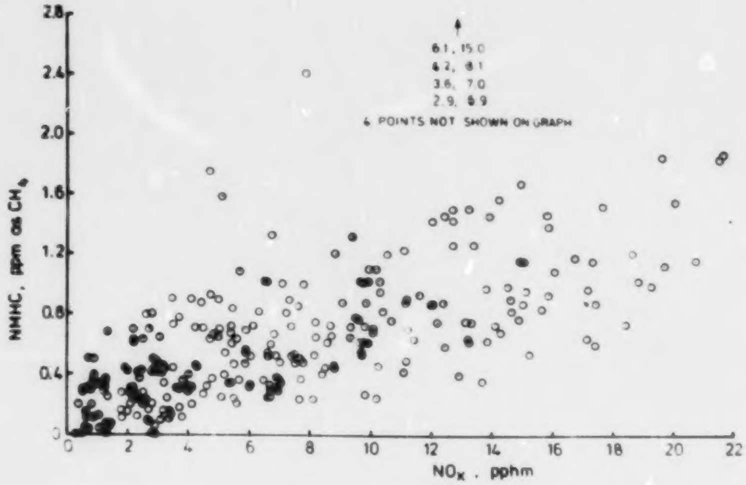

Figure 3. Half hour average NMHC and NO_X (0600 to 0900).

The emissions inventory given by Iverach and Bilger (1975) includes emissions from auto exhaust, crankcase blowby, and evaporation, as well as refinery, distributed solvent evaporative, and stationary combustion emissions. The automobile components are computed using factors estimated for Australian motor vehicles and using traffic volumes and speed from a Sydney-wide traffic survey. An analysis of the November and December 1975 precursor observations (Allen, 1976) shows that there is no statistically significant correlation of the observed ratio of NMHC to NO_X with a ratio predicted using upwind emission from the inventory for each measurement site. The median through the distribution indicates that the predicted ratio is about thirty percent higher than observed. Recent emissions laboratory tests of Australian motor cars show that the original automobile emissions factors used in the inventory are probably too high for hydrocarbon emission and too low for NO_X, and this fits with the observed ratio. Adjustments to stationary source emissions factors may also need to be taken into account. The inventory grid size, which in this case was two miles, is another factor which could influence the outcome of comparisons between measurements and inventory predictions, and this needs further investigation.

The measurements from March 19, 1976 have been chosen as a typical day illustrating the relation between concentrations predicted from the emissions inventory and measured values. On this day there were putative health effects (reported breathing pains in children exercising), peak ozone concentration was recorded near noon at 0.23 ppm, and visibility was reduced to a few hundred metres where the peak ozone was recorded. The measurement record (Figure 4) shows ambient concentrations of O_3, NO, and NO_2, with wind velocity indicated at the top of the figure.

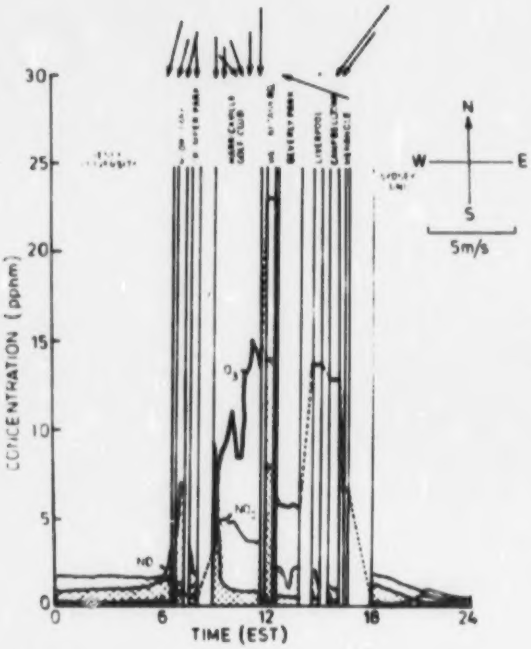

Figure 4. Measurement record for March 19, 1976.

In these observations, the 0900 to 1200 readings were downwind of the Silverwater source, 1200 to 1400 values were in sea breeze and were consequently lower, and after 1400 the mobile laboratory was driven inland to rejoin a trajectory computed from surface winds and high values were again recorded.

The morning build up of ozone is plotted in Figure 5 and compared with the predicted concentrations from the Eschenroeder and Martinez (1972) DIFKIN program adapted for Sydney conditions (Allen and Bilger, 1976). Following Eschenroeder and Martinez, the predicted NO$_x$ emission has been reduced by a factor of 4 and NMHC by 2 to better approximate the measured values. Observed ozone levels fell at the onset of the sea breeze and this is not shown by the model, since the model presently cannot handle conditions of wind shear and strong mixing.

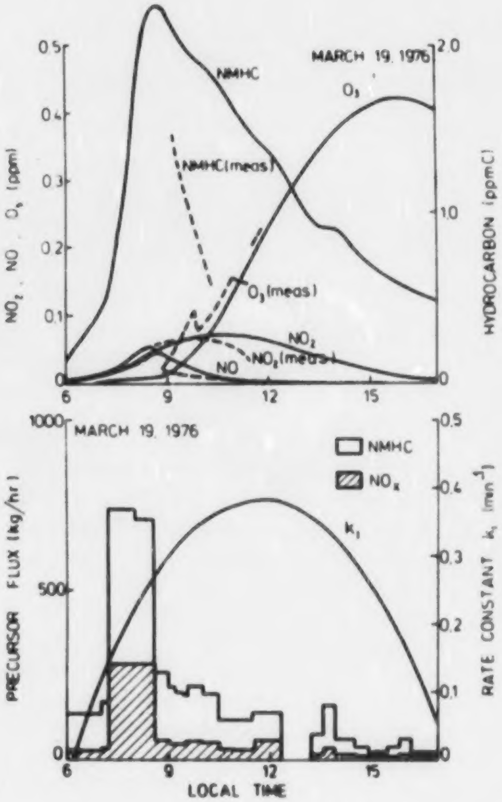

Figure 5. Precursor emissions and predicted ground level concentration of NO$_2$, NO, O$_3$ and NMHC.

The measured precursor concentrations have been used to compute an effective source strength (Table 1) using a surface mixing layer height of 300 m (measured at Silverwater at 1100 by the Macquarie University group) and wind speed 1 m/s average. The emissions are assumed to have become uniformly distributed through this layer over a two-mile square cell and the air was assumed to be clean before passing Silverwater, 11 km upwind. The source strength represents emissions into the trajectory from Silverwater to the measurement site over a period of approximately three hours. In comparison, the source strengths from averaging the emissions inventory along the trajectory are greater by a factor of two to four. The source strengths fall with time from 0900. This may be due to chemical reaction, but is more likely associated with dilution in a deepening surface layer.

TABLE 1. HOURLY AVERAGE NMHC AND NO_X AND COMPUTED SOURCE STRENGTH DOWNWIND OF SILVERWATER, MARCH 19, 1976

Time	NMHC ppmC	NO_x ppm	Computed NMHC source kg/4 sq. mile/3hr	Computed NO_x source kg/4 sq. mile/3hr
0900	0.65	0.065	1220	400
1000	0.57	0.063	1080	390
1100	0.34	0.045	640	280
1200	0.23	0.028	430	170
average source given by inventory			2400	820

All attempts to resolve the anomaly of the predicted concentrations from emissions exceeding measured concentrations using the known mixing layer depth have been unsuccessful. On other days, downwind from the petrochemical plants at Silverwater before 0700 ozone transients to 0.1 ppm have been observed following high transient NMHC concentration. At these times high $NMHC/NO_X$ ratios have been observed (greater than 50) and a purple brown haze was usual. The high concentrations were followed on December 12, 1976 about twenty kilometres downwind and higher than normal NMHC, ozone, and nitrogen dioxide concentrations were found. The observation of high ozone concentrations within an hour of sunrise is evidence for highly reactive hydrocarbon reactions. This chemical activity is not typical of photochemical smog production from auto exhaust where the reaction may take several hours to produce high ozone levels, and all of these observations have been traceable back to areas where there is a petrochemical industry.

The identification of the C.B.D. as a major emission source is more difficult than for refinery and industrial areas, and there are two main reasons for this. The distribution of the traffic is not over such a small area as with industry, even in the C.B.D. The ambient levels of NMHC and NO_X are consequently lower even though the same mass of pollutants may have been emitted. The second reason is that the peak traffic emissions occur at about the same time as the surface inversion breaks so that the ambient levels of the pollutants are lower and not as easily distinguished from other emissions. Ambient levels from stationary sources are usually higher since they can be measured before the inversion breaks and they generally originate from well-defined areas.

OZONE PRECURSOR RELATIONSHIPS

The development of ozone-precursor relationships from aerometric data requires a very large amount of data. In the EPA study used to develop the correlations shown in document AP-84 (1971), data from some thousands of days were analysed. These data were, however, for fixed site monitoring stations and the envelope correlations shown represent a very few points. Because these points represent maximum ozone for minimum precursor concentrations, it is probable that they correspond to days when dilution due to burning off the ground-based inversion occurred early in the day so that the smog development was not affected by later dilution, and that the days were relatively calm so that the ozone was not transported from the monitoring sites.

In the present study correlations will be developed between downwind maximum ozone and near-to-source morning precursor concentrations. Accordingly, much less data will be needed to establish an envelope relationship. Furthermore, by using the precursor concentrations existing around 0900 hours, when most of the dilution has already occurred, correlations which are comparable to the EPA envelopes, the Japanese correlations, and smog chamber data should be obtained. The amount of reaction of NMHC and NO_x that has occurred by this time will be small.

Table 2 shows data compiled in this way for six days over this last summer. A perfect trajectory relationship between sites for the precursor and the ozone have not been obtained in each case but they should be close. The data are plotted in Figures 6 and 7 to show correlation against NO_x and NMHC separately and then jointly. It can be seen that the data lie well within the envelope curve developed by the EPA for hydrocarbons and within the smog chamber curve reported by Pitts (1976) for the effect of NO_x. The 0.49 ppm C curve of Pitts lies close to the AP-84 envelope curve for correlation against NO_x. On the joint correlation only the four points having ozone close to 14 pphm are plotted. It can be seen that these four points show good correlation with the Pitts (1976) data and the EPA AP-84 envelope curves. However, they lie at quite a lot lower NO_x and NMHC values than would be expected from the Japanese data. It should be reiterated that there are several questionable features about using this data in this way. Also there are not enough results at this stage to draw any conclusions with regard to control strategy. It is hoped that the accumulation of much more data in the 1976-77 season will make the picture clearer.

TABLE 2. OZONE PRECURSOR RELATIONSHIPS

Date	NO_x pphm	NMHC ppm	Site	Time	Ozone pphm	Site	Time
30/10/75	7.3	1.0	Silverwater	0830-0850	14	Belmore to Liverpool	1300-1400
27/11/75	2.5	0.63	Concord	0900-0920	4.0	Belmore	1140-1240
1/12/75	4.4	0.93	Leichhardt Park	0930-0940	14.4	Canterbury	1020-1100
30/1/76	7.4	0.56	Centennial Park	0900-0940	14	Lidcombe	1200-1300
27/2/76	10.1	0.67	Leichhardt Park	0820-0900	8	Bankstown	1400-1430
19/3/76	6.2	0.85	Marrickville Golf Club	0910-0950	13.8	Liverpool	1430-1450

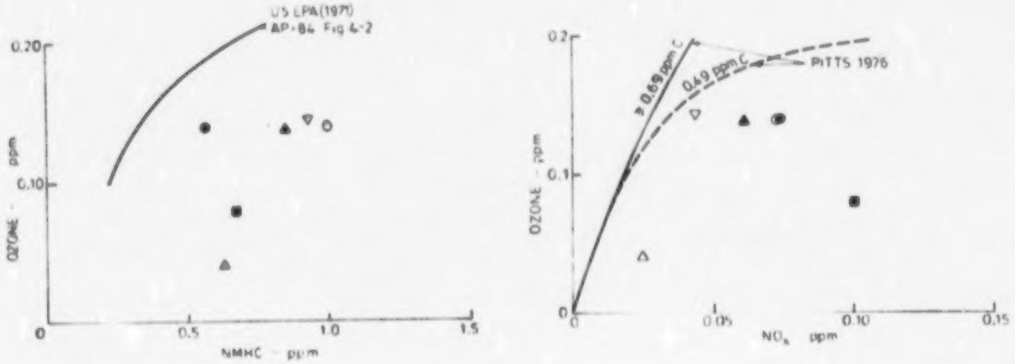

Figure 6. Downwind maximum ozone concentration as a function of (a) original upstream NMHC concentration and (b) original upstream NO_x concentration.

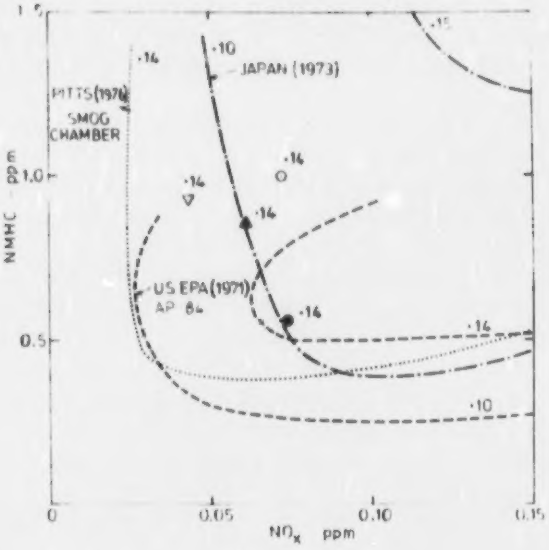

Figure 7. Peak ozone concentration as a function of upstream NMHC and NO_X concentration. Data shown is for Sydney, October 1975 to April 1976 and the dashed lines show correlations derived from both ambient and smog chamber data (see references).

CONCLUSION

Accurate measurements of ozone and precursors of photochemical smog have been made from a mobile laboratory. This method of operation for collecting data on reacting species has the advantage that the same set of instruments can follow a polluted air mass through an urban area, and sites can be chosen to avoid any local source effects. The chemiluminescent analysers proved to be stable and reliable under these conditions; however, there still remain problems with the hydrocarbons monitor operation.

The concentrations of NO_X and NMHC precursors have been found to be considerably lower (by a factor of 4) than is predicted from emissions inventories and dispersion models. This anomaly is still unresolved.

In general the NMHC/NO_X ratios are around 10, but under some conditions the ratio groups are closer to 4. It has not yet proved possible to correlate the NMHC/NO_X ratio with apparent sources. The inventories of source emissions are not well-defined and for some sources, such as oil refineries, the estimates of emissions could be too high.

The precursor concentrations on high ozone days are in relatively low ranges (0.4 - 1.0 ppmC NMHC and 0.02 - 0.10 ppm NO_x) compared with Los Angeles experience, but are still consistent with available data on ozone formation.

The first step in future work in the project must be the resolution of the anomaly between measured precursors and the values predicted from inventories. More data will also be collected to establish the relationship between precursors and ozone formation.

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SMOG-POTENTIAL OF AMBIENT AIR, SAMPLED AT DELFT, NETHERLANDS: THE EFFECT OF INCREASING NO_x CONCENTRATION

J. van Ham and H. Nieboer*

ABSTRACT

Effects of increasing precursor emissions on the formation of photochemical air pollution have been determined by experimental simulation, making use of ambient air collected at Delft, Netherlands. The smog-potential of early-morning air samples was compared with that of samples of the same day in which the nitrogen oxides concentration had been increased 50% by means of addition of nitric oxide. In our experiments, nitrogen dioxide maxima on an average increased proportionally with nitrogen oxides precursor concentration; for ozone maxima a 10-15% increase was found for a 50% increase of nitrogen oxides. It is argued that these results, which relate to a source around the sampling site measuring about 10,000 km², are indicative for the trend of photochemical air pollution in the Netherlands.

INTRODUCTION

Photochemical air pollution in the Netherlands has been documented since 1966 (1). There have since been several incidents of high concentrations of ozone (max. conc. 200 ppb) and peroxyacetylnitrate (PAN) (max. conc. 16 ppb) (2). Recently, peroxybenzoylnitrate (max. conc. 4.6 ppb) has also been identified as an air pollutant in the Netherlands (3). There is some concern about this type of air pollution because of resulting material and vegetation damage, including crop decreases, and in view of possible health effects.

In this respect it is of interest that the nitrogen oxides (NO_x) emission density in the Netherlands is one of the highest in the world (4).

The Rijnmond area, with its extensive petrochemical activities, is at the same time a powerful source area for hydrocarbons. The high traffic density in this part of Holland has been estimated to contribute 22% and 30% of, respectively, NO_x and C_xH_y emissions (5).

An increase in emissions will influence precursor concentrations and may result in a change of the average ratio of hydrocarbons to nitrogen oxides. The effect on photochemical air pollution of such changes is complex; the question of a relationship between precursors and oxidants has been a matter of discussion for many years (6), and it still appears to be thought-provoking (7).

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In order to establish relations between precursors and ozone, monitoring results as well as smog-chamber experiments have been used in several independent studies. In monitoring studies (8), maximum daily one-hour average oxidant concentrations were related to 6-9 a.m. average concentrations of total hydrocarbons minus methane and/or total nitrogen oxides. This approach, though of some value in urban areas, where automotive traffic is the main source of precursors, has been criticized (8) because it does not account for advection of precursors and oxidants after 9 a.m.

Moreover, it appears that on account of calibration problems in NO_x measurements, the relations obtained are probably in error (9). Relations between precursors and oxidants obtained from smog-chamber experiments are most often based on studies of systems containing mixtures of precursors, oversimplified in comparison to outdoor air. An approach in which an emission inventory is coupled with a chemical/transmission mathematical model appears to be a promising tool for establishing the causality pattern of precursor/ozone relationships and the consequences of various emission "scenarios". Such an approach that, apart from input data from the Netherlands, should also take into account emission contributions from adjacent European countries, is at present still far from its realization.

Another tool to predict the influence of emission changes is experimental simulation; it studies the effect of changing the precursor concentrations or their ratio on the smog-potential of ambient air. In 1973 we reported on a technique for performing this type of measurements (10). Measurements of smog-potential of ambient air have been carried out by several investigators (11, 12, 13, 14, 15, 16). As far as we know, a systematic investigation of the effect of increasing precursor concentrations on smog-potential of ambient air has not been published. Results obtained in a study on the effect of a 50% increase in NO_x emission on photochemical nitrogen dioxide (NO_2) and ozone formation will be reported here. Next, the significance of these results for the boundary layer will be discussed.

EXPERIMENTAL

SAMPLING

Samples were collected in Tedlar bags (80 l.) mounted in PVC containers. Air was taken in at 1.50 m above ground level by evacuating the container through a critical orifice. With the aid of a time switch, three 6-9 a.m. air samples of 65-70 litres were obtained at a time.

SELECTION

Samples were irradiated only if one of the following concentration limits was exceeded: 50 ppb NO_x, 5 ppb acetylene, or 5 ppb propylene. When there had been rain during sampling, or in the preceding hours, samples were discarded.

ADDITIONS

Nitric oxide was added by photolyzing NO_2 emitted by a permeation tube in a slow stream of dry nitrogen. Car-exhaust gas was added after dilution with nitrogen. The exhaust gases are those produced by a BMW 2000 running a driving cycle according to ECE 15.

IRRADIATION

The air samples were irradiated in the Tedlar sampling bags in special carts provided with TL-05 tubes (Philips). The spacial light intensity within each cart amounted to 100 W/m^2, measured by the ONBA-method (17). Owing to temperature fluctuations, variations in light intensity up to 5 percent were noted; they are insignificant in this comparative study. The irradiation in most experiments lasted 6 hours.

TEDLAR REACTORS

The reactors were conditioned as described earlier (10); this resulted in the formation of minor amounts of ozone on irradiation of purified air. Reactors were discarded when the blank ozone production exceeded 10ppb/hour. The ozone concentrations mentioned in this paper have been corrected for "blank ozone". Decomposition of ozone at the walls of the reactor has been established. We assume that this loss of ozone is equal in bags of the same age and with identical sampling histories.

MONITORING

Nitric oxide and NO_2 were measured by a Picos (manufactured by Hartmann and Braun). Ozone was measured according to Lindqvist (18). C_2-C_5 hydrocarbons were measured after having been concentrated (19). Peroxyacetylnitrate was measured as described earlier (2).

RESULTS

Between September 1972 and February 1974, 40 samples of ambient air, selected after analysis, were--with and without additions--irradiated in the laboratory.

CHARACTERIZATION OF THE AIR SAMPLES

The measurement of precursor concentrations in the samples revealed that a division could be made into three source categories. To this end, NO_x, ethylene (E), acetylene (A) and propylene (P) were taken as source indicators.

In car-exhaust gas, prepared according to the European test cycle, we found that the ratio $\frac{10\ ([E] + [A] + [P])}{[NO_x]} = 4.8 \pm 1.3$.*

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*Average of six tests with a BMW 2000. The average ratio C_xH_y (in ppm C_6)/NO_x in the exhaust gas amounted to 2.1 ± 0.1. For the ratio C_xH_y/NO_x in exhaust gas of seven cars of different makes and types, an average value of 1.92 was found.

Under highway driving conditions, this ratio lies between 0.2 and 0.4. Moreover, city traffic is characterized by a ratio [E] : [A] : [P] = 1 : 1 : 0.25; the [E]/[A] ratio may vary, depending on driving conditions, between 0.7 and 1.4.

By these characteristics, samples fell into three categories. One was of predominantly city-traffic origin; the second had important industrial hydrocarbon contribution ([E] / [A] ~2; [P] / [A] 1); the third category was rich in NO_x, indicating highway-traffic emissions and/or contributions from heating furnaces or power stations as the predominant sources. The average composition of the samples in each category is summarized in Table 1.

TABLE 1. AVERAGE CHARACTERISTICS OF SAMPLES FROM DIFFERENT SOURCE CATEGORIES

source category*	n†	NO_x ppb	[E] / [A]	$\frac{10([E] + [A] + [P])}{[NO_x]}$	Average windspeed during sampling m/sec.
I	11	159	1.0	5.3	1.85
II	14	92	4.6	13.1	1.8
III	12	197	1.4	1.6	3.0

* I = city traffic, II = industrial, III = rich in NO_x

† is number of experiments

The origin of the samples was also checked from the wind direction during the sampling period; the sample categories matched the various source areas very well. This is shown in Figure 1. This finding enables us to compare smog-potentials of samples originating from different source areas.

SMOG-POTENTIAL

A typical result of the irradiation of ambient air is reproduced in Figure 2.

The following data of the oxidant components, e.g. ozone, may serve as a measure for the smog-potential:

- the maximum concentration : $[O_3]$max (ppb)
- the irradiation time required to reach maximum concentration : t_{max} (O_3) (min)
- the integrated dosage (concentration x time) : n-hours-O_3-dosage (ppb hour)

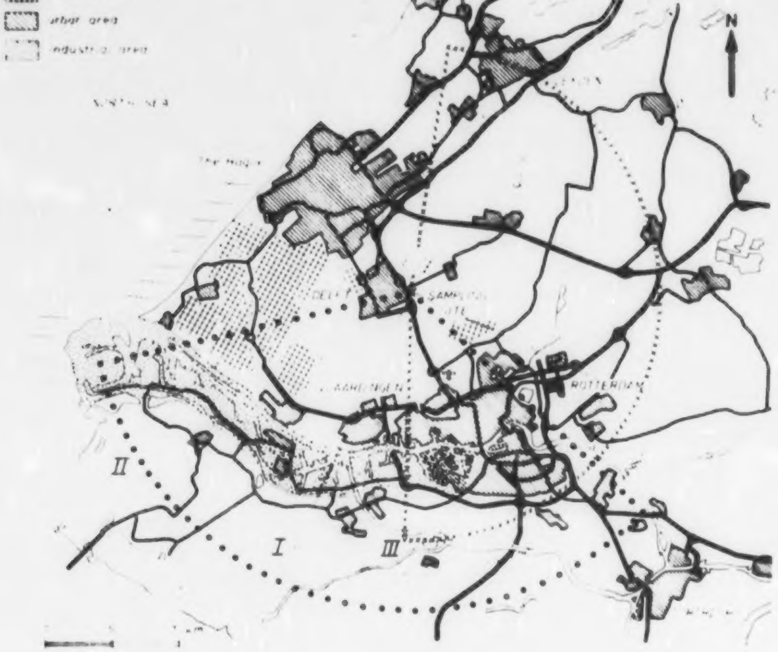

Figure 1. Map of southwestern part of the province of South Holland; source areas of precursors in air sampled at delft.
I = City Traffic ; II = Industrial ; III = Rich in NO_x .

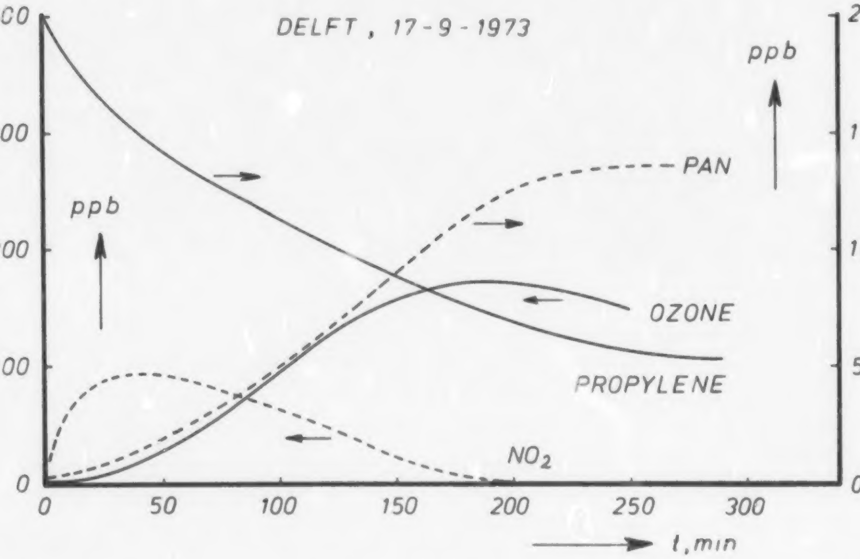

Figure 2. Smog profile of an ambient air sample irradiated in the laboratory.

The figures obtained have been averaged per source category; differences in ozone data among the three categories appear from Table 2.

TABLE 2. AVERAGES OF PARAMETERS FOR OZONE FORMATION IN THREE SOURCE CATEGORIES

Source	N*	$t_{max.}$ (O_3) min.	$[O_3]$ 3 hours ppb	$[O_3]$ max. ppb	3-hours O_3-dosage ppb hours	4-hours O_3-dosage ppb hours
City Traffic	10	238	103	180	202	396
Industrial	14	198	105	149	243	351
Rich in NO_x	12	>295*	62	183*	116	241

n* is number of experiments

* In this category, several ozone maxima were not reached within the six hours of irradiation. Averages were obtained by substituting the end-value of ozone or the total irradiation time. Therefore, the figure in the table is too low.

EFFECT OF INCREASING NO_x CONCENTRATION ON SMOG-POTENTIAL

A typical effect on the smog-potential of an addition of NO is illustrated in Figure 3.

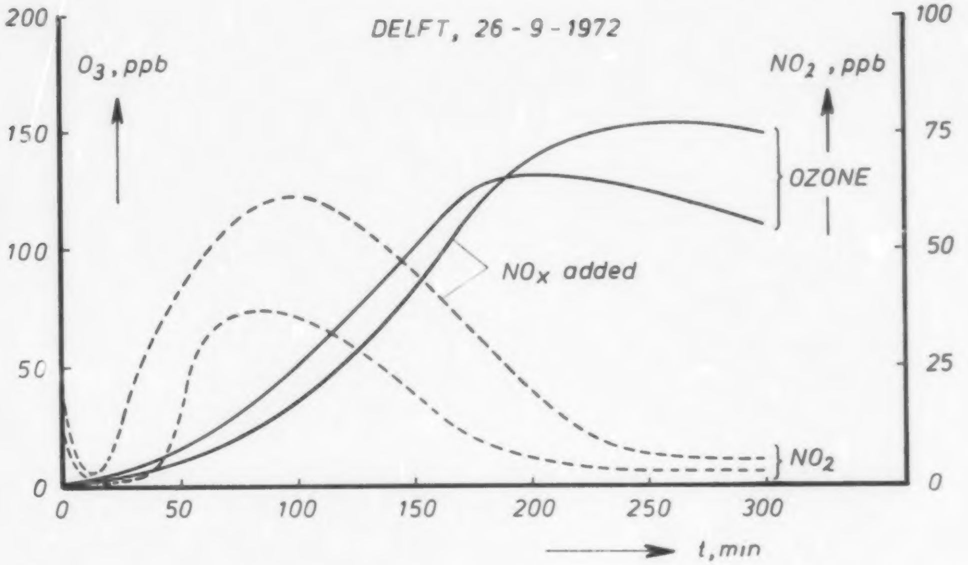

Figure 3. Formation of NO_2 and O_3 in ambient air irradiated under standard conditions.

The effects have been expressed as ratios of corresponding quantities of the spiked sample and of the control sample. These ratios have been averaged. Table 3 shows ratios for several characteristics of the smog potential on addition of NO, averaged per category with standard deviation.

TABLE 3. AVERAGE EFFECT (WITH STANDARD DEVIATION) ON FORMATION OF NO_2 AND O_3, WHEN NO_x-CONCENTRATION WAS INCREASE 45%, IN THREE CATEGORIES OF AMBIENT-AIR SAMPLES

Source	Number	$\frac{[NO_2]\ max^{+}}{[NO_2]\ max^{o}}$	$\frac{4\text{-hours-}NO_2\text{-dosage}^{+}}{4\text{-hours-}NO_2\text{-dosage}^{o}}$	$\frac{t_{max}[O_3]^{+}}{t_{max}[O_3]^{o}}$
city traffic	10	1.44 ± 0.09	2.15 ± 0.38	1.16 ± 0.06
industrial	9	1.32 ± 0.07	2.15 ± 0.53	1.25 ± 0.20
rich in NO_x	8	1.54 + 0.09	1.62 + 0.16	>1.24*

Source	Number	$\frac{[O_3]\ 3\ hour^{+}}{[O_3]\ 3\ hour^{o}}$	$\frac{[O_3]\ max^{+}}{[O_3]\ max^{o}}$	$\frac{4\text{-hours-}O_3\text{-dosage}^{+}}{4\text{-hours-}O_3\text{-dosage}^{o}}$
city traffic	10	0.97 ± 0.07	1.09 ± 0.04	0.92 ± 0.06
industrial	9	1.06 ± 0.11	1.14 ± 0.04	0.91 ± 0.07
rich in NO_x	8	0.49 + 0.10	>1.10*	0.60 + 0.05

* In the spiked samples, the ozone maxima had not been reached at the end of the experiment; a higher average is probable.

PAN formation has been measured in a few experiments only. For the "city traffic" category, some examples of the effect of NO addition on the PAN maximum are presented in Table 4 and compared with O_3 maxima in the same experiments.

DISCUSSION

The smog-potentials of ambient air in the "city traffic" and "industrial" categories (Table 2) were found to be such that ozone maxima appeared on the average after 3 to 4 hours of irradiation. The integrated light dose after 4 hours' irradiation is the equivalent of a half summerday's sunshine in the Netherlands.

TABLE 4. PAN AND OZONE-MAXIMA IN SOME SAMPLES OF AMBIENT AIR AND THE EFFECT OF NO-ADDITIONS

Date	[PAN] max, ppb		$[O_3]$ max, ppb	
	Control sample	Spiked sample	Control sample	Spiked sample
21-11-'73	22	29	-	360
20-12-'73	15	18	212	184
19- 2-'74	10	15	160	200

The "rich in NO_x" samples need some more time. It appears that the emission situation, as far as represented in the samples under investigation, is on the average favourable for the formation of photochemical smog. In this respect, the "rich in NO_x" samples carry less weight than the other categories because they occur predominantly in the winter half-year. At our latitude, oxidant formation by photochemical processes is then negligible owing to the lower light intensity. Samples from the other two categories are more or less distributed over the whole year. Early-morning sampling is a necessary condition for obtaining samples whose precursors composition has not yet been altered by chemical reaction. It would be of interest to check whether the average composition of emissions which accumulate below the radiation inversion during the night and early morning differs considerably from that of a 24-hour day. We have thus far confined ourselves to a crude inventory of emissions; it indicates that two major sources will generally not be represented in early-morning samples:

- hydrocarbons evaporation losses from storage tanks: evaporation is promoted by insolation and occurs mainly between 8 a.m. and 2 p.m.;
- nitrogenoxide emission from high sources: the radiation inversion is often not dissolved until 9 a.m., thus preventing stack emissions to mix with the surface layer.

This supports our assumption that the average ratio of hydrocarbons/nitrogen oxides in the samples does not differ much from the ratio of the emissions of a natural day. Moreover, the samples were collected under a variety of wind directions so that the resulting collection of samples covered widely diverging hydrocarbons/nitrogen oxides ratios. This is of importance, as it justifies the assumption that the average effect of NO_x additions on the smog-potential of the early-morning samples equals the effect on a hypothetical sample containing a proportional part of the average emissions during 24 hours.

The most pronounced effects of future increase in NO_x emission on smog-potential are summarized in Tables 3 and 4, which give averages for a collection of experiments with 45% NO_x increase. These effects are:

- proportional increase of NO_2 maximum and NO_2 dosage;
- increase in maximum ozone concentration;
- increase in maximum PAN concentration: the effect for PAN is possibly more pronounced than for ozone;
- lengthening of time-period needed to reach NO_2 maximum and ozone maximum;
- decrease of ozone formation after short irradiation times, corresponding with the lengthening of t_{max} (O_3); a marked effect in $[O_3]_{3\ hours}$ is only visible in the "rich in NO_x" category.

In order to translate these effects in terms valid for the free atmosphere, the role of factors that have not been incorporated in our experiments has to be assessed. In the boundary layer, wind and convection are important; moreover, emission of precursors is a continuous process. Of these factors, continuous emission and dilution are counteracting and partly compensating processes, and in our comparative experiments they have been left out of account.

Vertical transport, which is primarily responsible for dilution, may have another effect during smog episodes. It is now well documented (20) that ozone formed in smog episodes during the day may persist overnight above a radiation-inversion layer. The next day, the ozone is mixed with new precursors, accelerating chemical reactions which lead to photochemical smog.

We wish here to point out that our comparative experiments also afford the best practical approximation to obtain the average effect of changes in precursor composition on the concentration of ozone persisting overnight. Most relevant in this respect are the effects on $[O_3]_{max}$, which were tabulated in Table 3.

We expect that the retarding effect of extra NO_x will be counteracted when more ozone from aloft, also resulting from the extra NO_x, is available for mixing.

At the present moment, a quantitative evaluation of this effect is not yet possible, owing to insufficient knowledge of atmospheric processes, expecially that of mixing of air parcels after disappearance of an inversion layer.

For this reason, the effects on the ozone-dosages in ambient air may ultimately turn out different from those found in the smog chamber. However, the effects on the ozone concentration and, more specifically, the ozone maxima indicate the trend of photochemical air pollution for the chosen emission scenario.

Horizontal transport of air parcels, from which the samples have been taken, causes the ozone concentrations to reach their maxima at distances from the emission area that vary with windspeed. Consequently, the average effects found concern an area around the sampling site of about 10,000 km^2 (based on the mean wind velocity during the night before sampling). The ozone above a nocturnal inversion undoubtedly originates from emissions in a still larger area.

Summarizing, it may be noted that our technique is useful especially when a combined chemical-transmission model is not available, and when an increase in precursor emissions is expected. On the basis of an estimated 50% increase in NO_x emission in the Delft area within the next 5-10 years, a 10-15% increase in severity of photochemical smog is to be expected, at least for those days when its formation is "favoured" by the weather.

ACKNOWLEDGEMENTS

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A PRELIMINARY INVESTIGATION OF EXPECTED VISIBILITY IMPROVEMENTS IN THE LOS ANGELES BASIN FROM OXIDANT PRECURSOR GASES AND PARTICULATE EMISSION CONTROLS

C. S. Burton, T. N. Jerskey, and S. D. Reynolds*

ABSTRACT

Results are presented describing the improvements in visibility, sulfate, organic, primary particulate, and total aerosol concentrations that can be expected for different emission control alternatives in the Los Angeles Air Basin. The importance of giving proper attention to photochemical secondary aerosol formation is indicated, which in turn points to the improvements in visibility and total suspended particulates with concomitant reductions in ozone concentrations. The importance of treating the total air quality system (gases and particulates) in designing and evaluating visibility and sulfate control strategies is emphasized.

INTRODUCTION

It is well recognized that in addition to high oxidant concentrations, another manifestation of smog in the Los Angeles Basin (LAB) is reduced visibility. Furthermore, it is obvious that visibility reduction is the most generally recognizable form of air quality degradation. For cloud-free conditions, the optical properties of the atmosphere are in general determined by the light absorption by gases and scattering by suspended particulates. In the Los Angeles Basin however, recent field studies have often shown that the measured particle volume concentration in the range 0.1-1.0 μm (diameter) is correlated well with the extinction due to scattering by particles as measured with an integrating nephelometer(1). This observation is consistent with Mie scattering theory and, for the Los Angeles Basin at least, indicates the relative unimportance of light absorption by particles and gases. Additional measurements have also shown that the 0.1-1.0 μm size range encompasses one mode (mass mean diameter 0.4-0.8 μm) of a usually observed bimodal volume distribution(1,2). Furthermore, chemical analyses have often shown that a dominant influence on both the aerosol mass concentration of this mode and visibility reduction is secondary aerosol--nonmaritime sulfates, nitrates, and organics formed in the atmosphere as a result of a complex series of gas-to-particle conversion processes(1,3-6). Of these materials, accumulated evidence suggests that the sulfate mass fraction of the total aerosol mass is the most important single aerosol constituent affecting visibility on a per unit mass basis(6).

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The physical and chemical mechanisms responsible for secondary aerosol formation are still to be characterized in a manner as detailed as secondary gas formation. Nevertheless, for the Los Angeles Basin, accumulated evidence implicates the homogeneous gas phase reactions rather than the heterogeneous reactions as being the most important(1,7,8). Correlations between sulfate and organic aerosol concentrations with ozone levels implicate various portions of the NO_x-hydrocarbon oxidation reaction mechanism as being the most important.

It is qualitatively apparent from the foregoing, therefore, that there are a myriad of potential emissions control options for improving visibility, including fine particle emissions control, SO_2 emissions control, and control of oxidants via control of hydrocarbons and nitrogen oxides precursor emissions. In particular, improvements in visibility can be expected in the future from oxidant control programs already underway. However, the best single or mixed control strategy has not been apparent, and is in part the subject of the work reported here.

In this paper it is our purpose to describe briefly the adaptation of the Systems Applications, Inc. (SAI) Urban Airshed Model to include secondary aerosol formation and the prediction of visibility (visual range). We then use this planning tool to examine the effects on visibility improvements for the Los Angeles Basin for various control strategy options. These options include (a) continued oxidant control to meet the ozone standard with and without further reductions in sulfur dioxide (SO_2) and primary particulates and (b) no further oxidant control from current levels, but additional SO_2 and primary particulate emission controls. We emphasize that the findings of this part of the investigation are preliminary, in that further verification of the various elements of the analysis is necessary and for each control scenario greater resolution in the degree of control should be carried out. We also emphasize that the results are limited to the Los Angeles Basin.

ANALYTICAL APPROACH

The analytical approach taken in this study consisted of three parts:

- Prediction of the mass concentration of the principal aerosol components (sulfate, organic, nitrate, and primary particulates) in the Los Angeles Basin for a typical smoggy day using a numerical grid-type model(9).
- Calculation of the visibility in four-square-mile cells using a relationship between the visual range and the aerosol scattering coefficient(10), and a linear relationship between the aerosol scattering coefficient (b_{scat}) and the mass of each component of the aerosol derived from data collected in the California Aerosol Characterization Experiment (ACHEX) for the Los Angeles Basin(1).
- Application of the model to various control strategies including nitrogen oxides (NO_x), hydrocarbon, SO_2, and primary particulate reductions.

Application of this methodology, which will be described in more detail shortly, is well suited for establishing the relationship between emissions of primary pollutants and the expected levels of deleterious products, in particular secondary pollutants. It provides both spatial and temporal distributions of both the primary pollutants and their products, and the effect of controls on the concentration of primary pollutant as well as secondary pollutants.

In this study 1975 was taken as the base year. A day was selected with meteorology typical of conditions that would occur on a smoggy day in the late summer or early autumn. For the appropriate 1975 emissions, visibilities were calculated for each four-square-mile area. Then reductions in ambient concentrations of SO_2, primary particulates, and ozone were made so as to meet various desired concentrations and the visibilities for each grid square computed. The desired reductions in ozone concentrations led to reductions in the nonmethane hydrocarbon and NO_x concentrations. It should be noted that the maximum ground-level concentration, which occurs in different places in the Los Angeles Basin, was used to determine the desired percentage reduction.

In the following paragraphs our methodology is described in greater detail.

RELATING VISIBILITY TO MASS AND AEROSOL COMPOSITION

Meteorological range or visibility is defined as the distance at which a standard object can just be distinguished from the background. Koschmeider (10) found that the visual range, L_v, could be expressed in terms of the extinction for light scattering by the relation

$$L_v = k \left(b_{scat}\right)^{-1} \tag{1}$$

where b_{scat} is in units of $10^{-4}\ m^{-1}$. Values of k have been determined theoretically and empirically. For the former, for a homogeneous atmosphere, k is 3.9 for an ideal black target, while for less than ideal targets a value of 2.9 is appropriate. Empirical values determined in California range from 2.27 to 3.37. In this study we used k = 2.9.

Of those field studies establishing relationships between b_{scat} and aerosol mass, the results of the ACHEX study are the most useful. Statistical analysis of two-hour average aerosol composition, relative humidity, and corresponding b_{scat} measurements provided a relationship between b_{scat} and the mass concentration of sulfate, nitrate, total aerosol mass, and relative humidity. The relationship is given by

$$b_{scat}\left(10^{-4}\ m^{-1}\right) = 0.02\left(M_T - M_S - M_N\right) + 0.062\ M_S + \left(0.020 + 0.049\mu^2\right)M_N \tag{2}$$

where M_T, M_N and M_S are the total mass, nitrate mass, and sulfate mass, respectively (all in units of $\mu g\ m^{-3}$), and μ denotes the fractional relative humidity. In using Equations 1 and 2 to relate the calculated mass concentrations of the constituents of the aerosol to the visual range, we:

- Utilized model total mass, sulfate, and nitrate results averaged over a two-hour period and a 2x2 mile spatial average.

- Assumed a 50 percent relative humidity.

THE NUMERICAL MODEL

The numerical model used to predict the aerosol species concentrations was a modified version of the grid-type Eulerian model described by Reynolds et al.(9). The model solves the species transport equations

$$\frac{\partial c_i}{\partial t} + u \cdot \nabla c_i = \nabla \cdot (K \nabla c_i) + R_i + S_i, \qquad (3)$$

subject to boundary conditions which are described in Reynolds et al.(9). In Equation 3, c_i is the concentration of species i, u denotes the wind vector, K is the mass diffusivity, R_i is the net rate of production (possibly negative) of species i, and S_i denotes the source term. In the model's normal operation, the concentration of each species or group of species is determined by the solution of the set of transport equations that are coupled through the reaction terms. For this study, the transport equations were solved only for SO_2, sulfates, organic aerosol, and primary particulates. The other species involved in the chemical reactions, nonmethane hydrocarbons and ozone, were obtained from measurements and were not predicted. By doing this we avoided computational errors and reduced the cost of applying the model. Nitrate aerosol concentrations were not predicted by the model but were included in the total mass by a method described below. Background aerosol concentrations can be included in the model through initial and boundary conditions; however, for this application background concentrations were simply added to the total calculated mass prior to the calculation of the visibility.

Wind vectors and mixing depths are required inputs to the model for the entire time period for which the model is run. September 30, 1969 was chosen from the days available because of the relatively high pollutant concentrations measured on that day and because the wind patterns were typical of many late summer and early autumn days in Los Angeles. The meteorology for that day was used in all the computer simulations described in this report.

Two basic assumptions were made regarding the formation of secondary aerosols:

- Formation of each species of secondary aerosol occurs independently of the primary aerosol present and the rate of formation of the other species.

- Steady-state concentrations of condensable materials exist in the gas phase so that the rate of formation of condensable material in the gas phase is equal to the rate of formation of condensed material.

The validity of these assumptions has been discussed(11). It follows immediately from these assumptions that all condensable material produced in the gas phase is converted to secondary aerosol.

Of the possible paths available for sulfate aerosol formation(12,13), available field data for the Los Angeles Basin and elsewhere indicate the significance of the indirect photooxidation mechanism for converting SO_2 to sulfates(1,12). For this mechanism the reactive species HO·, RO·, $HO_2^{\cdot}$, $RO_2^{\cdot}$ and $O(^3P)$ are responsible for oxidizing SO_2 to sulfur trioxide (SO_3), so that assuming the reaction of SO_3 with water vapor is sufficiently rapid and the concentration of water vapor is sufficiently constant, the rate of formation of sulfate is given by

$$d[SULF]/dt = [SO_2] \sum_i k_i[R_i] \quad , \tag{4}$$

where R_i denotes the reactive species i and k_i is a rate coefficient which is a function of the water vapor concentration. Since these same reactive species are related to the concentration of ozone, we assume that Equation 4 can be expressed as

$$d[SULF]/dt = k_1[SO_2][O_3]^\gamma \quad , \tag{5}$$

and will approximately represent the rate of formation of sulfate. Roberts (14) has used sulfate and SO_2 data from the Los Angeles Basin to calculate values of k_1 for $\gamma=1$. The mean value obtained by Roberts, used herein, was 0.72 ppm^{-1} hr^{-1}. The mean molecular weight of sulfate of 125 g $mole^{-1}$ was used to calculate the mass concentration of sulfate(1).

Accumulated laboratory and field observations indicate that ozone and higher molecular weight olefinic materials produce traces of particulate matter. Neither the nature of the particulate materials nor the reactive species that are important is well established, although it is reasonably certain that 1:1 adducts of ozone and an olefin are not important(7,13). Based on what is known, an appropriate form of the reaction rate might be

$$d[ORG]/dt = \sum_{i,j} k_{ij}[RHC_i][R_j] \quad , \tag{6}$$

where k_{ij} is the reaction rate coefficient, $[RHC_i]$ is concentration of nonmethane hydrocarbon producing organic aerosol, and $[R_j]$ denotes the concentration of the transient reactants. Following the same reasoning as used in obtaining Equation 5 from Equation 4, we have

$$d[ORG]/dt = k_2[NMHC]^\alpha[O_2]^\beta \quad . \tag{7}$$

Grosjean and Friedlander(7) provide data from which k_2 can be estimated to be 0.2 ppm^{-1} hr^{-1} for $\alpha=\beta=1$. This value together with an average molecular weight of 159 g $mole^{-1}$ was used in calculating the mass concentration of aerosol.

There is virtually no quantitative information available on the rates of conversion of NO_x to nitrate in the atmosphere, albeit many possible paths exist. In the ACHEX study, no systematic, useful relation could be established between observed nitrate concentrations and those of ozone, nitric oxide (NO), NO_2, sulfate, relative humidity, or noncarbonate carbon(1). The method of estimating the nitrate concentration employed here was to assume that it represented 8 percent of the aerosol mass for the base case year of 1975. For other years the nitrate level was rolled back according to reductions in NO_x emissions.

Calculation of the secondary aerosol emissions utilized 1975 emissions for September and measured ozone and nonmethane hydrocarbon concentrations. Primary aerosol emissions were calculated from mobile carbon monoxide (CO) emissions and stationary SO_2 emissions by multiplying by the corresponding emissions factors(15). We assumed no change in these factors between 1973 (for which they were tabulated) and 1975 (for which they were applied). The SO_2 emissions inventory was updated to September 1975 by contacting power stations in the Los Angeles Basin. Finally, following Trijonis et al.(16), a two-hour average background concentration of 44 $\mu g\ m^{-3}$ was assumed.

THE VARIOUS SCENARIOS

Various scenarios were selected to compare the 1975 visibility levels with those that would exist under conditions of reduced oxidant and SO_2 concentrations. The method used to correct hydrocarbon, ozone, and nitrate levels was based on rollback using a modeling analysis developed by the Los Angeles County Air Pollution Control District (LAAPCD)(17,18). Originally, the following four scenarios were proposed:

- The 1975 base case;
- The 1975 base case, but with SO_2 emissions rolled back to meet the 0.04 ppm California 24-hour standard;
- The 1980 oxidant, NO_x, and nonmethane hydrocarbon concentrations predicted by the LAAPCD method for the same meteorology as the 1975 base case;
- The 1980 case above, but with SO_2 emissions rolled back to meet the 0.04 ppm 24-hour standard.

After studying the results from the above scenarios, two more cases were added:

- A yearly maximum oxidant level of 0.16 ppm and the corresponding NO_x and nonmethane hydrocarbon determined by the LAAPCD method with no SO_2 rollback;
- The case above, but with SO_2 emissions rolled back to meet the 0.04 ppm 24-hour standard.

SUMMARY OF APPROACH

Ideally the visibility model would include all the phenomena and all the inputs listed in Figure 1; however, because of the limited level of effort in this study, not all of the inputs or physical phenomena were adequately treated. We have outlined the approach above; in Table 1 we summarize our assumptions.

RESULTS AND CONCLUSIONS

Using the approach discussed in the previous section we have examined the effect of reducing SO_2 and ozone concentrations on visibility within the Los Angeles Basin. The results presented in this section illustrate the following points:

- Although the sulfate aerosol contributes more on a per weight basis to the visibility reduction, sulfate, in general, represents less than 30 percent of the aerosol mass and contributes less to visibility reduction than the other components.
- Since a reduction in oxidants reduces the concentrations of all of the secondary aerosols, greater improvements in visibility can be made by controlling oxidants than by controlling SO_2.
- Controls on the large stationary sources (power plants and refinery operations), which are generally regarded as significant sources of SO_2 emissions, appear to have a relatively minor effect on sulfate concentrations.
- Our results suggest that the current California visibility standard could not be met even by the implementation of controls that would result in achievement of both the Federal oxidant standard and the California 24-hour average SO_2 standard (even if extreme controls were placed on emissions of primary particulates).

The information available from this modeling approach is extensive and cannot be presented within the space allotted here. Tables 2 and 3 summarize the "worst case" visibilities for the various scenarios considered in this study. Without controls on primary particulates, the best visibility which could be achieved was 6.4 miles with a yearly maximum one-hour concentration of 0.09 ppm O_3 and a maximum 24-hour average SO_2 concentration of 0.04 ppm. The composition of the aerosol in this case is dominated by the primary particulates. Table 3 shows the effect of reducing the primary particulate concentration by one-third or two-thirds. As expected, the most significant improvement in visibility occurs when the precursors of secondary aerosols are at their lowest concentrations. In this case, the "worst case" visibility increases from 6.4 miles to 7.8 miles with a two-thirds reduction in primary particulates. Hence, controls that would reduce the yearly maximum one-hour

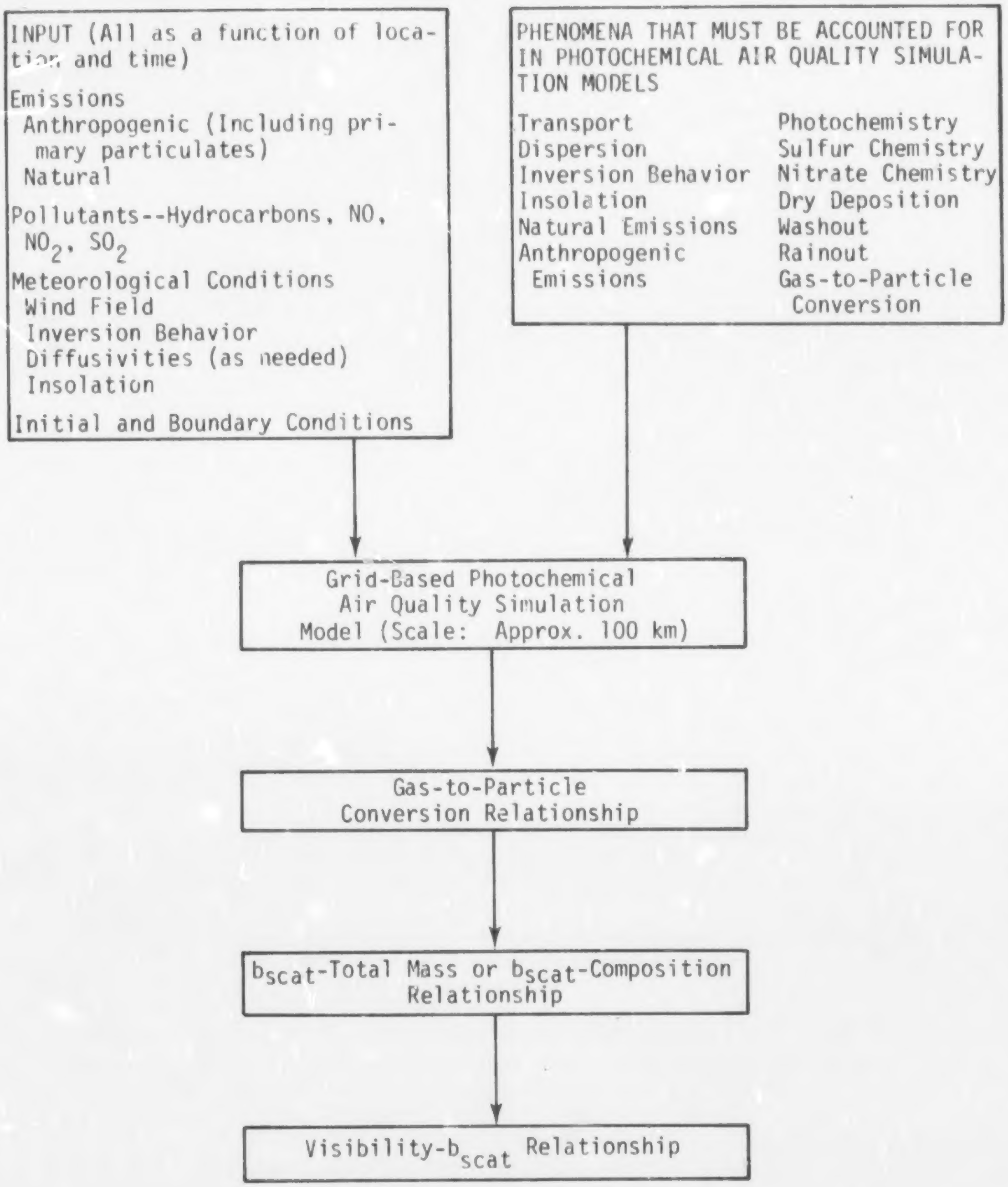
INPUT (All as a function of location and time)
Emissions
Anthropogenic (Including primary particulates)
Natural
Pollutants--Hydrocarbons, NO, NO_2, SO_2
Meteorological Conditions
Wind Field
Inversion Behavior
Diffusivities (as needed)
Insolation
Initial and Boundary Conditions
PHENOMENA THAT MUST BE ACCOUNTED FOR IN PHOTOCHEMICAL AIR QUALITY SIMULATION MODELS
Transport
Dispersion
Inversion Behavior
Insolation
Natural Emissions
Anthropogenic Emissions
Photochemistry
Sulfur Chemistry
Nitrate Chemistry
Dry Deposition
Washout
Rainout
Gas-to-Particle Conversion
Grid-Based Photochemical Air Quality Simulation Model (Scale: Approx. 100 km)
Gas-to-Particle Conversion Relationship
b_{scat}-Total Mass or b_{scat}-Composition Relationship
Visibility-b_{scat} Relationship

Figure 1. Components of a visibility prediction model.

TABLE 1. ASSUMPTIONS OF OUR APPROACH

(1) The meteorological variables correspond to 30 September 1969.

(2) The rates of formation of sulfate and organic aerosol from the gas phase are assumed to be proportional to the concentrations of SO_2 and nonmethane hydrocarbons, respectively. The rate constant in each case is assumed to be proportional to the ozone concentration.

(3) The nitrate aerosol concentration is assumed to be 8 percent of the total aerosol mass for the base case year [approximately the proportion found in ACHEX (California Aerosol Characterization Experiment)]. The gas-to-particle conversion of this component is not modeled.

(4) Ozone and nonmethane hydrocarbon concentrations are not predicted by the model; they are interpolated for the year 1969 from APCD measurements. These 1969 concentrations were extended to 1975 using Los Angeles County APCD worst-case projections.

(5) A linear rollback technique is applied to the hydrocarbon, ozone, and nitrate concentrations using hydrocarbon, NO_x, and ozone worst-case projections given by the Los Angeles County APCD for the base case year (1975) and other scenarios.

(6) This rollback is assumed to occur without a shift of the maximum ozone concentration in space or in time.

(7) The formation of secondary aerosol and its rate of condensation on particles is assumed to be independent of the composition of the aerosol present.

TABLE 2. EFFECTS OF VARIOUS CONTROL STRATEGIES ON SECONDARY AEROSOL COMPOSITION, TOTAL MASS, AND VISIBILITY AT THE LOCATION OF MINIMUM VISIBILITY

Scenario	Aerosol Mass ($\mu g\ m^{-3}$) Sulfate	Organic	Nitrate	Primary	Background	Total Mass	b_{scat}, $10^{-4}\ m^{-1}$	Visibility (miles)	Visibility (mi) with a Background Concentration of 100 $\mu g\ m^{-3}$
Base Case (1975):									
without SO_2 control	61	86	21	58	44	270	8.2	3.4	2.9
with SO_2 control	45	86	20	58	44	253	7.2	3.9	3.3
Predicted Results for 1980; Meeting 0.09 ppm O_3 Yearly Maximum Ozone Concentration:									
without SO_2 control	39	13	11	61	44	168	5.1	5.5	4.3
with SO_2 control	27	15	11	58	44	155	4.4	6.4	4.9
Predicted Results for 1980; Meeting 0.16 ppm O_3 Yearly Maximum Ozone Concentration:									
without SO_2 control	47	22	15	61	44	189	5.9	4.7	3.9
with SO_2 control	34	22	15	61	44	176	5.1	5.5	4.3

TABLE 3. EFFECTS OF PRIMARY PARTICULATE CONTROLS ON VISIBILITY AT THE LOCATION OF MINIMUM VISIBILITY

	Aerosol Mass			
Scenario	Primary ($\mu g\ m^{-3}$)	Total Mass ($\mu g\ m^{-3}$)	b_{scat}, $10^{-4} m^{-1}$	Visibility (miles)
1975 Ozone Concentrations without SO_2 control:				
1/3 prim*	39	251	7.8	3.6
2/3 prim+	19	231	7.4	3.8
with SO_2 control:				
1/3 prim	39	234	6.8	4.1
2/3 prim	19	214	6.4	4.4
1980 Meeting 0.09 ppm Yearly Maximum Ozone Concentration				
without SO_2 control:				
1/3 prim	41	148	4.7	5.9
2/3 prim	20	127	4.3	6.5
with SO_2 control:				
1/3 prim	39	136	4.0	7.0
2/3 prim	19	116	3.6	7.8
1980 Meeting 0.16 ppm Yearly Maximum Ozone Concentration				
without SO_2 control:				
1/3 prim	41	169	5.5	5.1
2/3 prim	20	148	5.1	5.5
with SO_2 control:				
1/3 prim	41	156	4.7	5.9
2/3 prim	20	135	4.3	6.5

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* Primary particulates reduced by 1/3

+ Primary particulates reduced by 2/3

average ozone concentration to 0.09 ppm, allow the California SO_2 standard to be met, and reduce primary particulates by two-thirds, would not result in the attainment of the present California visibility standard.

These results also show that a more significant reduction in aerosol mass and a corresponding improvement in visibility can be achieved by reducing ozone concentrations than by limiting emissions of SO_2 from large stationary sources. This result is observed even when the ozone is reduced only enough to meet a maximum hourly average concentration of 0.16 ppm. Under this condition, without SO_2 control the aerosol mass is reduced by 30 percent whereas SO_2 control only reduces the mass by an additional 7 percent.

ACKNOWLEDGMENTS

In the course of this project we have benefitted greatly from discussions and criticisms of several colleagues. In particular, we appreciate the valuable comments of Drs. P. M. Roth and G. Z. Whitten of SAI and Drs. Attaway, Greenfield and Peyton of Greenfield, Attaway, and Tyler. We also wish to express our appreciation to P. M. Mundkur and J. Ames for carrying out the computer calculations. This study was carried out under contract to Greenfield, Attaway, & Tyler, San Rafael, California, as part of a larger study to examine various pollutant control strategies in the Los Angeles Basin.

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SESSION 20

CONTROL OF OXIDANT PRECURSOR EMISSIONS - I

Chairman: R.W. Bilger
University of Sydney, Australia

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TRAFFIC MANAGEMENT AS A MEANS OF OXIDANT PRECURSOR CONTROL FROM LOW-SPEED SATURATED TRAFFIC

R. B. Hamilton and H. C. Watson*

ABSTRACT

In large cities, automobiles contribute significant quantities of photochemical oxidant precursors, and the driving sequence can effect motor vehicle emissions. Previous studies have concentrated on reducing carbon monoxide by traffic control. This report shows that average speed is the determining factor for hydrocarbon emissions, with acceleration rates largely determining nitrogen oxides emissions.

Traffic density profiles in some large cities have been found to be similar. Vehicle miles of travel per unit area are highest in the central business district area and fall exponentially, being 50% less at a 2 ml radius. Conversely, average traffic speeds increase with increasing distance from the central business district. Average speeds and vehicle halts per mile are closely related. Based on our vehicle emission test data, city traffic management through improved traffic flow can reduce hydrocarbon and nitrogen oxides emissions in central business district areas by 48% and 66% respectively. Steady-state driving, the ideal, would give a nitrogen oxides reduction of approximately 70-90%. A 50% reduction of hydrocarbon and nitrogen oxides in the two-mile square around the central business district would reduce about 25% of the total automotive precursor emissions in the greater city area.

The upgrading of manual fixed cycle traffic signal systems can be done at a modest cost and result in overall community savings of time, accidents, energy, and reduced photochemical oxidant emissions in the critical central business district area.

INTRODUCTION

At the beginning of automotive emissions control it was recognized that driving sequences can affect vehicle emissions. Thus, emissions have been regulated according to measurements made over prescribed driving schedules. Rose et al. (1) demonstrated that carbon monoxide (CO) and hydrocarbon (HC) emissions were sensitive to the average speed at which the vehicle is driven, but they were unable to define a speed influence on nitrogen oxides (NO_x) emission.

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While recent works (2, 3, 4, 5) have quantified how changing traffic patterns influence CO emissions, little effort appears to have been expended in optimizing traffic management to minimize the oxidant precursors HC and NO_x.

In this paper we enumerate how the vehicular emissions source varies in the city road network, show which areas give rise to greatest oxidant precursors, and propose control policies with simple traffic control measures rather than complex optimal controls. Projections of the effects of traffic management have been applied to traffic streams in which vehicles are without NO_x emission control, since it is only with the implementation on July 1, 1976 (Australian Design Rule 27A) that NO_x emission have been regulated to approximate U.S. 1973 light vehicle levels, and thus the emission characteristics of controlled vehicles in Australia have become available to us only recently.

The forecasts made in this paper are founded on two earlier investigations:

- The development of an empirical model which simulates the instantaneous emissions from vehicles which are representative of the population average.
- A preliminary investigation into traffic patterns in Melbourne.

These investigations have been combined with an analysis of traffic density (VMT/m^2) data and associated average vehicle speed for some major cities.

VEHICLE EMISSIONS MODEL

The emission model is an updated version of that developed by Watson (7) and is available as a computer program called STEM-CA. Its essential features are that for each of four driving modes, acceleration, cruise, deceleration and idle (ACDI), the emissions concentration, c, and exhaust flow rate, q, are calculated from the instantaneous velocity, v, and acceleration, a:

$$q = q\ (v,a,m) \qquad (1)$$

$$c_p = c_p\ (v,a) \qquad (2)$$

when m is the vehicle mass and p = CO, HC and NO_x.

These expressions are combined with the pollutant density to calculate the mass emissions rate:

$$e_p = \rho q\ c_p \qquad (3)$$

The functions q and c_p are polynomial expressions in v and c whose coefficients have been determined by regression analysis of emissions measurements made in a baseline survey using U.S. 1970 Federal Test Procedure (FTP). Other details of the procedure have been documented by Bulach (8). Further details of the validation of STEM-CA may be found in Reference 9. Another program, STEM-CB, is available to calculate instantaneous mass emission rates from modal emission data by a constant volume sampler (CVS) method (US 1973 FTP), but requires further validation.

TRAFFIC PATTERN STUDY

In this preliminary study commenced in 1973 (10), a single route was selected that contained central business district (CBD), arterial, sub-arterial and freeway driving. The route was subdivided into 10 sections or links by major intersections, each section taking about 100 seconds of driving time.

Standard techniques were used and multiple runs were made during peak and offpeak hours to obtain a significant (10%) level of accuracy using the chase car technique (11, 12). All the data was manually digitized for subsequent computer analysis.

EMISSIONS-SPEED VARIATIONS

Input of the velocity (and acceleration by differention) records from the traffic pattern survey yielded values of emissions rates for a typical vehicle. Integration gave mass emissions on a distance or on a sectional basis. The HC and NO_x emissions from the typical vehicle in gm/ml as a function of average speed for each pass along each section in peak/offpeak traffic are shown in Figure 1(a) and 1(b). The HC emissions are strongly speed dependent over the 1.5 to 43 mph average speed range encountered. Regression analysis of these results gives the expression:

$$HC = 83.23/\bar{v} + 3.19, \text{ where HC is in gm and } \bar{v} \text{ is in mph.}$$

The correlation coefficient for this expression is $R = 0.96$. The remainder of the variation is the influence of changing accelerations from section to section.

Superimposed on these results, to establish credibility, are values from several baseline emissions surveys according to European (13), Australian (14), Japanese, and American (15, 16) test procedures. Where necessary, results have been factored by 1.65 to convert non-dispersive infrared HC values to flame ionization detector HC values, and adjusted to a common vehicle inertia mass of 2,820 lb wt. by assuming a linear relation between emissions and mass.

The corresponding variation of NO_x with average speed is shown in Figure 1(b). There is no simple dependence of NO_x emission on average speed. Emission rates at constant average speed can vary by as much as 3:1, depending upon acceleration rates. This variation will be discussed in more detail later in the paper.

URBAN TRAFFIC CHARACTERISTICS AFFECTING EMISSIONS

The source strength along a roadway is the product of the emissions per vehicle and the vehicle volume flow rate. We have just shown that the emissions rate is a function of speed and acceleration patterns. In saturated peak hour traffic, the volume flow rate is closely related to the average speed and is a function of a large number of controlling factors which may be satisfactorily simulated by 'queueing theory' (17). However, because of the complexity of such simulation, we have resorted to published data on traffic volume measurement to enable us to demonstrate the apparent generalities of urban traffic flow and driving patterns.

TRAFFIC DENSITY A FUNCTION OF CITY RADIUS

Vehicle miles of travel (VMT) have been quantified for Los Angeles by Roth et al. (18) and by the Sydney Transportation Study (19) for each grid square of the urban areas, using 2 mi separated orthogonal grid lines. The highest VMT occurs in the CBD and an analysis of these results to give VMT as a function of radius from the CBD are presented in Figure 2, together with Melbourne data from Smeed (20). The sophistication of the road networks in terms of greater or lesser proportions of freeways and the effect on road space demand as influenced by city size have been allowed for by normalizing both VMT and the radial distance, R:

$$VMT^{*} = MVT/VMT_{max} \text{ and } \qquad (5)$$

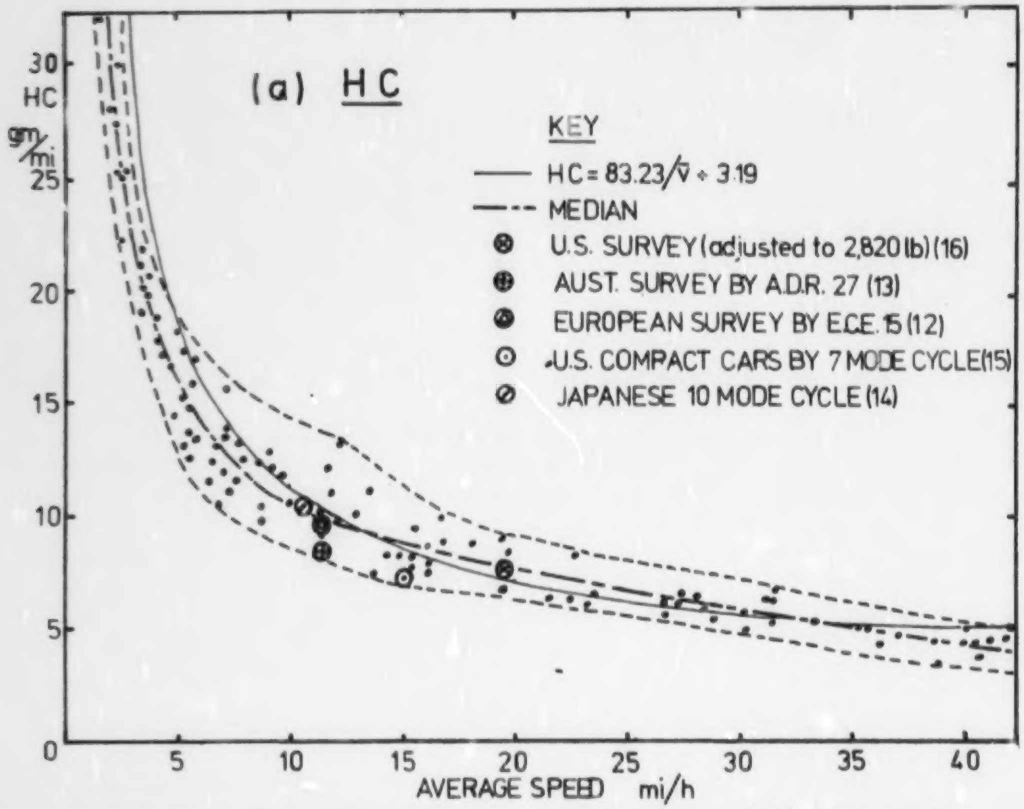

Figure 1a. HC and NO_x emissions predicted for Melbourne Route using STEM-CA program.

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*Smeed (2) has shown that the city area, A, varies as $A=P/500)^{0\cdot7}$, whence for circular cities $R = \sqrt{\frac{A}{\pi}} = \frac{1}{\sqrt{\pi}}\left(\frac{P}{500}\right)^{0.35}$.

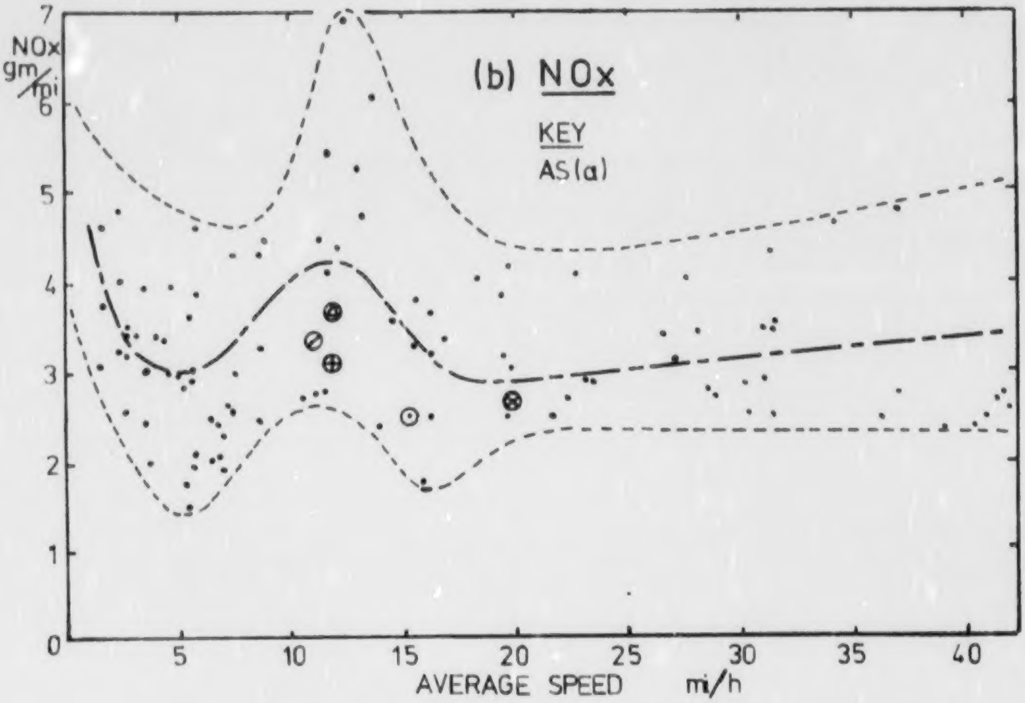

Figure 1b. HC and NO_x emissions predicted for Melbourne Route using STEM-CA program.

$$R = R_M \left(\frac{P_M}{P}\right) 0.35 \qquad (6)$$

where the maximum VMT, VMT_{max} and the population ratio of Melbourne to the other cities (P_M/P) can be found from Table 1.

TABLE 1. CITY DATA - TRAFFIC VEHICLE MILES PER DAY

	SYDNEY	LOS ANGELES	MELBOURNE
$VMT_{max}/ml^2/day$	177,000*	359,000	126,000
$P(x10^{-6})$	2.8	6.9	2.6

*Sydney a.m. peak = $15,130/ml^2/hr$

We conclude from Figure 2 that in central areas there is considerable similarity in the decrease in VMT with distance from the CBD with a 50% reduction within two miles. It will be noted also that the standard deviation between cities and the time of day (Sydney 24-hour data and a.m. peak hour) remains consistent. A generalization extended to all cities cannot be justified on the basis of the sample of three for which data was readily available, but warrants further study.

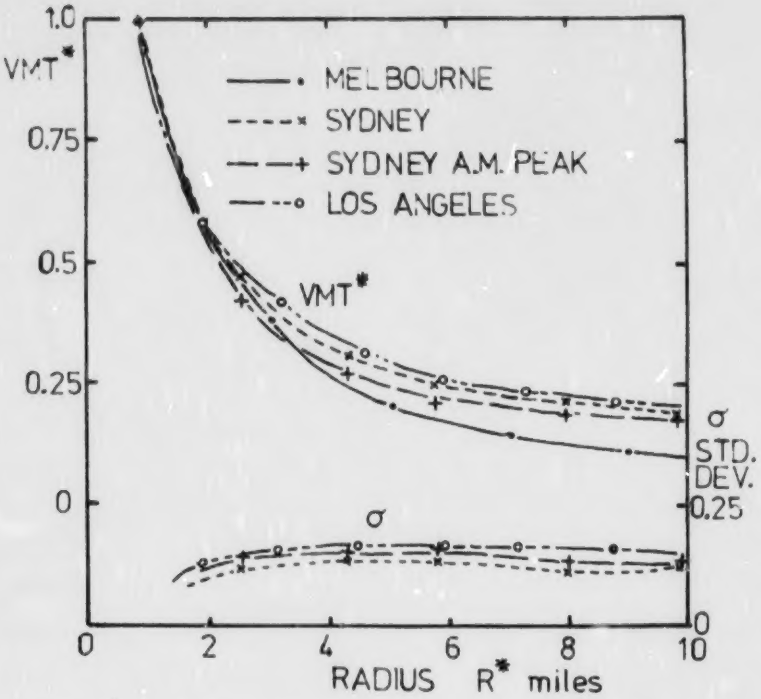

Figure 2. Normalized vehicle miles travelled (VMT) against normalized radius for 3 cities.

AVERAGE SPEED INCREASES WITH RADIAL DISTANCE

The variation in average traffic speed with increasing city radius is summarized in Figure 3 for Sydney (19), Melbourne (21) and London (22). There appears to be considerable similarity in the rising speed with radial distance for all three cities, and only small shifts in average speed occur between peak and offpeak conditions. The large difference in standard deviations at given radii between London and Sydney can be explained in terms of the different areas over which the speeds were averaged: city boroughs in London (2 to 40 ml^2) and 4 ml^2 grids in Sydney.

TRAFFIC PATTERNS CHARACTERIZED BY HALTS PER MILE

The simplest way of characterizing traffic patterns is in terms of halts/mile. Data from U.S. sources (23, 24), including industry and government driving cycles, are given in Figure 4(a) together with actual city and suburban driving measurements from the U.S. (12) and Australia, largely for Sydney (25) and our own for Melbourne (10). Halt frequency with average speed is remarkably consistent, except at speeds less than 10 mph where traffic flow is very congested. Agreement between the data from the same sources on idle time as a proportion of total trip time is less well-defined.

The constraints of roadway design, signal frequency driving codes, ve-

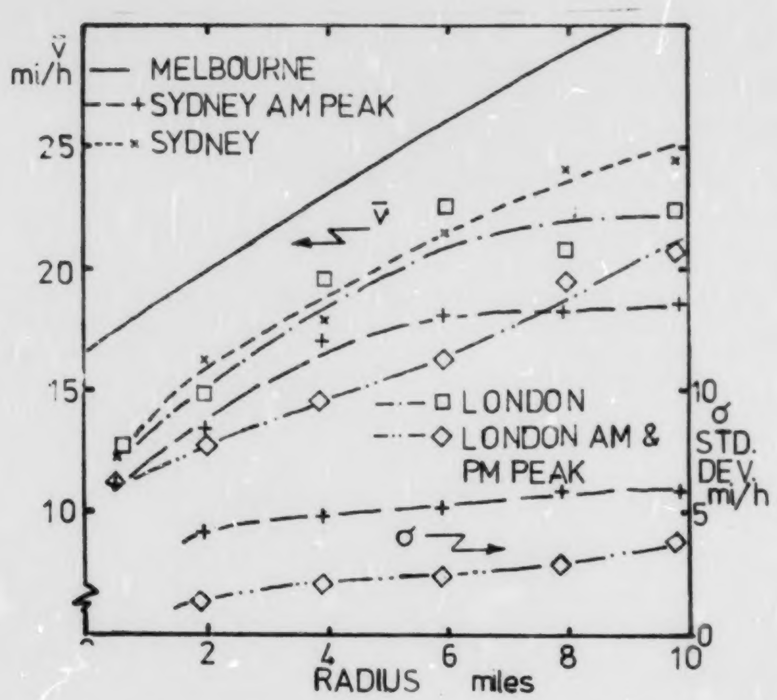

Figure 3. Vehicle average speed $\overline{V}$ as a function of radius for 3 cities.

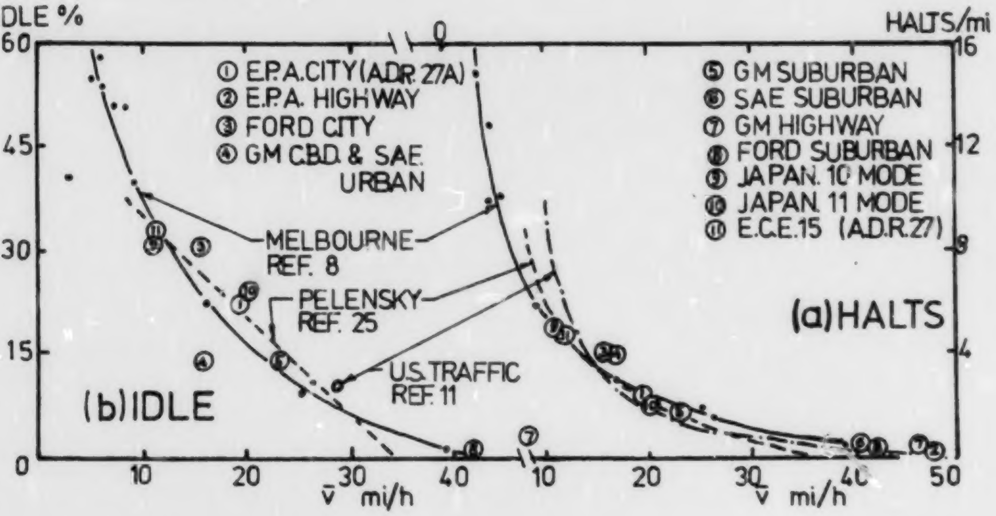

Figure 4. Halt frequency and idle % total travel time as functions of average speed for observed traffic and driving schedules.

hicle performance potential, and driver habits appear to give consistency in speed, halts frequency, and idle time, provided the averaging time is greater than 6 to 7 minutes. This represents the residence time of a vehicle in an area of high precursor emissions, which later results in an air mass of high oxidant potential.

SIGNIFICANT DIFFERENCES IN ACCELERATION RATES

Significant differences in the acceleration characteristic of traffic flow appear to exist within the overall constraints, and these can be expected to be reflected in differences in NO_x emissions. To illustrate this, the bivariate distributions of frequency versus acceleration, and velocity of our Melbourne measurements and the LA (E.P.A. City) cycle can be compared in Figure 5. There is only a small difference in average speed between the two driving patterns (3.5 mph), yet the HC and NO_x values predicted by STEM-CA for these schedules give higher NO_x for the Melbourne pattern, but lower HC. The HC are contrary to the expected change on the basis of the median lines of Figure 1(a) and (b), as can be seen from Table 2.

TABLE 2 COMPARISON OF EMISSIONS OVER LA-4 AND MELBOURNE DRIVING PATTERNS

	v(mph)	HC(gm/ml)	NO_x(gm/ml)
LA-4 cycle	19.6	7.60	2.58
Melbourne	16.1	6.23	3.19
Difference	3.5	+1.37(18%)	-0.61(24%)
Expected difference	-	-0.92(12%)	-0.30(12%)
Error		2.29(30%)	0.31(12%)

Further comparison between accelerations in Melbourne and the five U.S. City data (26) can be made in Figure 6.

The above examination of traffic patterns and emission consequences emphasizes the need to account for local patterns and intercity variations in the emissions. Effort may only be justified in predicting these variations when the modelling of the dispersion and chemical reaction components of ambient air quality forecasting becomes sufficiently precise to make the likely errors in source prediction unacceptable.

In this regard, it is likely that only a small section of the road network system needs detailed study using the concept of acceleration noise (11). In major Australian cities, about 50% of VMT occur on the arterial road network, i.e., approx 7% of the total urban network system (27).

EMISSIONS DISTRIBUTION WITHIN URBAN AREAS

Accounting only for the median effects of average speed on emissions (i.e., ignoring acceleration influences) for cars, it is possible to compute the distribution of the vehicular emissions source and its variance, knowing the

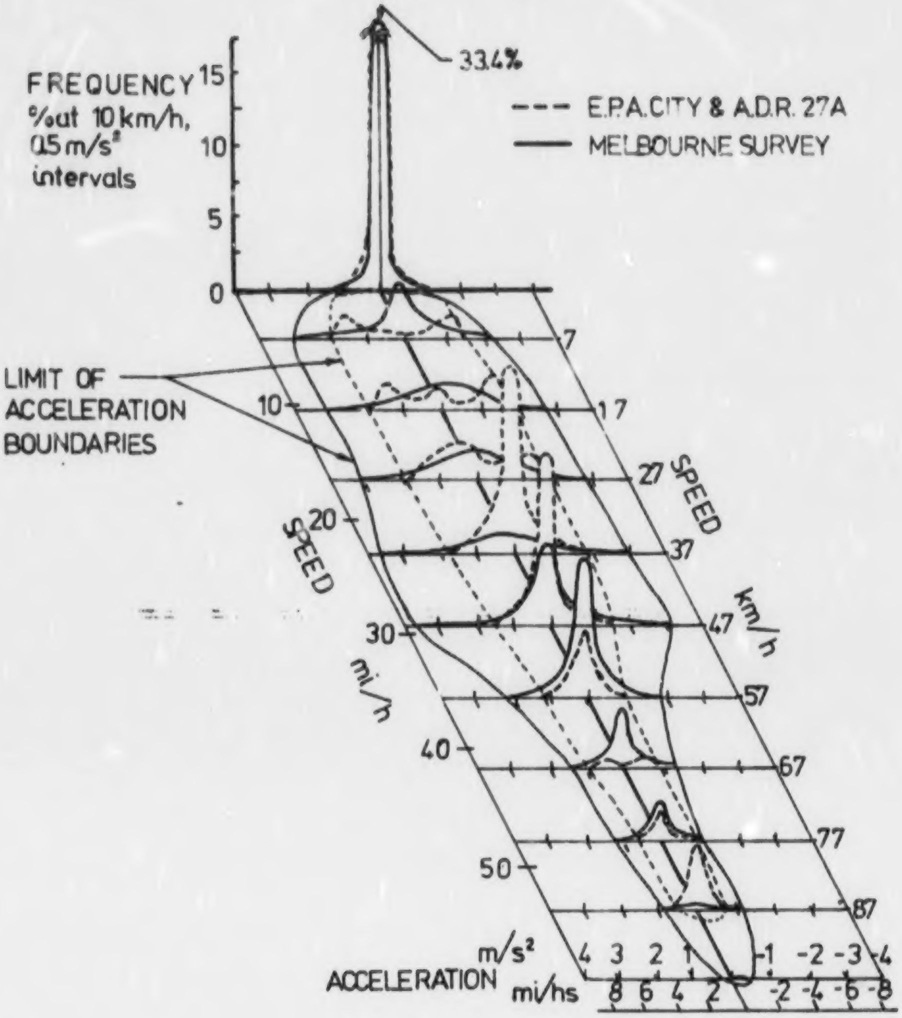

Figure 5. Bivariate frequency versus acceleration and velocity distribution of E.P.A. city (and Australian design rule 27A) and Melbourne survey (weighted according to total VMT on CBD road, arterial and freeways).

speed and VMT distributions as in Figures 2 and 3. It can be seen clearly from Figure 7 that the peak HC and NO$_x$ sources from motor vehicles arise in city centres. The emissions loading on the environment falls to one-half its maximum value at less than a 2 ml radius from the city centre. This fall is contrary to the expected constant HC and rising NO$_x$, emissions from the total traffic stream that can be expected in saturated traffic conditions as the speeds rise away from the city centre on a unit length of road (27).

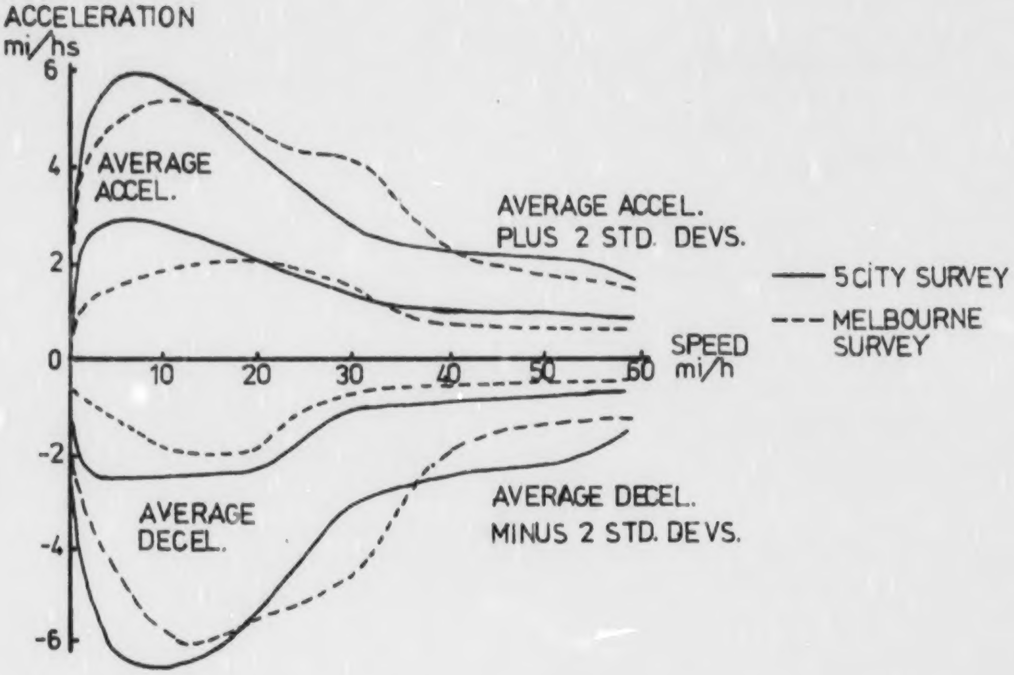

Figure 6. Comparison of acceleration velocity relations for Melbourne survey (weighted) and Scott Laboratories--5-city results.

CONTROL MEASURES TO REDUCE OXIDANT PRECURSORS

The city centre will be the highest source of oxidant precursors from the engine with a HC/NO_x ratio of about 2.7 to 3 for a non-emission controlled vehicle population (see Figure 7), and this is the region to which control strategies for mobile sources must be directed.

Control can be effected by the following, separately or in combination: exhaust emission limitation, traffic access restriction, and traffic management.

The driving pattern adopted in the U.S. and Australia for automotive emissions control (LA-4 cycle) has an average speed greater than that experienced in the central business areas of many large cities at peak hour, (usually 8-15 mph, LA-4 cycle 19.6 mph), as well as other differences pointed out above. Consequently, the emissions reductions achieved over the cycle may not be achieved under these low speed conditions. The results are of great practical significance, for the a.m. peak hour speeds are lowest in and around the CBD (27). In Sydney during the a.m. peak, some 60% of the VMT is less than 15 mph, with 69% less than 12 mph concentrated in the area around the CBD.

We have made appropriate modifications to STEM-CA to reproduce the NO_x emissions reductions that can be expected in Australia by the adoption of U.S. 1973 FTP (6). Industry has forecasted that this will bring about a reduction

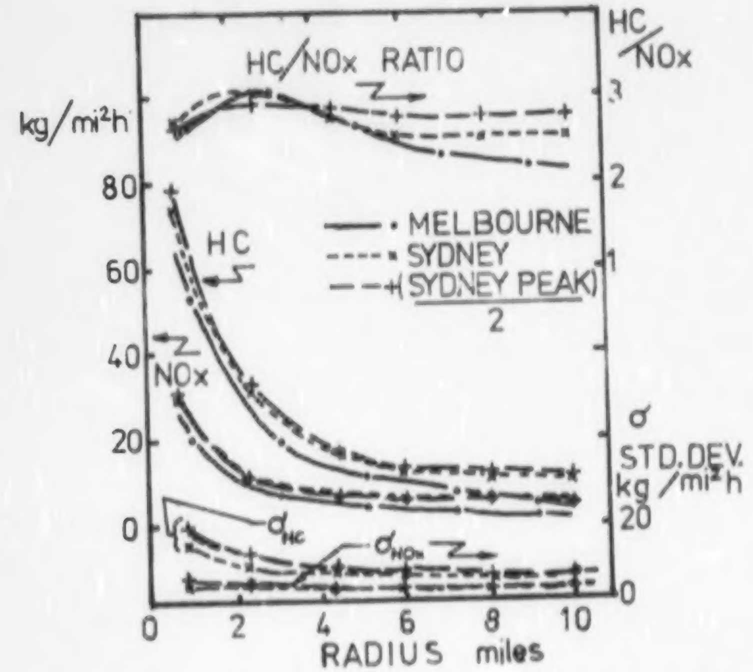

Figure 7. The HC and NO_x source intensity, their standard deviations and HC/NO_x ratio variation with city radius. Melbourne and Sydney 24-hour data and Sydney a.m. peak results.

of 38% (28) in NO_x emissions for the average vehicle. The forecast reductions that would be achieved over our Melbourne driving pattern can be seen in Figure 8. Over the speed range 10 to 24 mph, reductions will probably be better than the reduction achieved over the LA-4 cycle. Only at very low speeds, 2 to 4 mph, will 75% of the forecast reduction be achieved. With emissions-controlled vehicles, the emissions will tend to be highest at low speeds and hence worst in the CBD area.

In the Organization for Economic Cooperation and Development (OECD) countries, restricting traffic access to city centres has been carried out, but it is doubtful if traffic reductions by 50% over a sufficiently large area (10 ml^2) could be achieved initially with public and economic acceptability (29).

EMISSIONS CONTROL BY TRAFFIC MANAGEMENT

Traffic management techniques, as a primary NO_x control strategy, do appear to be practicable. Firstly, we examine in Figure 9 what reductions are already achieved in urban driving. The results of Figure 1(b) are replotted showing emission points on each of the 10 Melbourne sections for which the traffic flow was above 90% of the saturated traffic density, as defined by highway capacity manuals (17). By examining only saturated conditions, which apply at the a.m. peak hour, we are able to observe emission rates from driving that is restricted by road rather than restricted by driving habit, which is more difficult to draw useful conclusions from. In Figure 9, it is clear

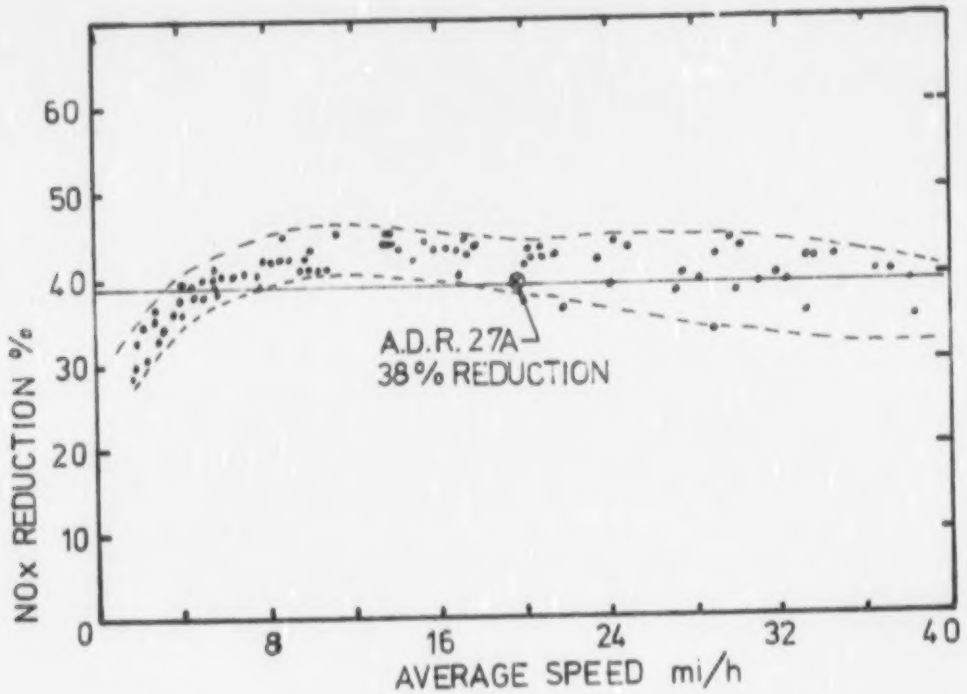

Figure 8. Predicted acheived NO_x emissions reductions from average vehicle over traffic survey speed range in Melbourne giving 38% reduction over ADR 27A (U.S. 1973 FTP).

that as average speeds increase, sections 4 and 6 have significantly less emissions than sections 3, 5 and 7. Also shown in Figure 9 is the emission rate that would be achieved at steady-state driving, which would be impracticable to maintain at low speed. The reductions actually compared to those possible are detailed in Table 3.

TABLE 3: NO_x EMISSION REDUCTIONS ACHIEVED IN DRIVING COMPARED TO BEST POSSIBLE BY STEADY-STATE DRIVING

Velocity Average mph	Best Pos. Reduction %	Reduction Achieved from Med. %	Redn.not Achieved of Poss. %	Median gm/ml	Min. Poss. gm/ml	Min. Obs. gm/ml	Achieved Reduction gm/ml
2	65	9	86	3.3	1.2	3.0	0.3
4	79	28	42	2.9	0.6	2.1	0.8
8	89	58	35	3.8	0.4	1.6	2.2
12	90	60	34	4.2	0.4	1.7	2.5
16	74	50	40	3.2	0.52	1.6	1.6
20	76			2.8	0.68		
26	68			3.1	1.0		
36	42			3.3	1.9		

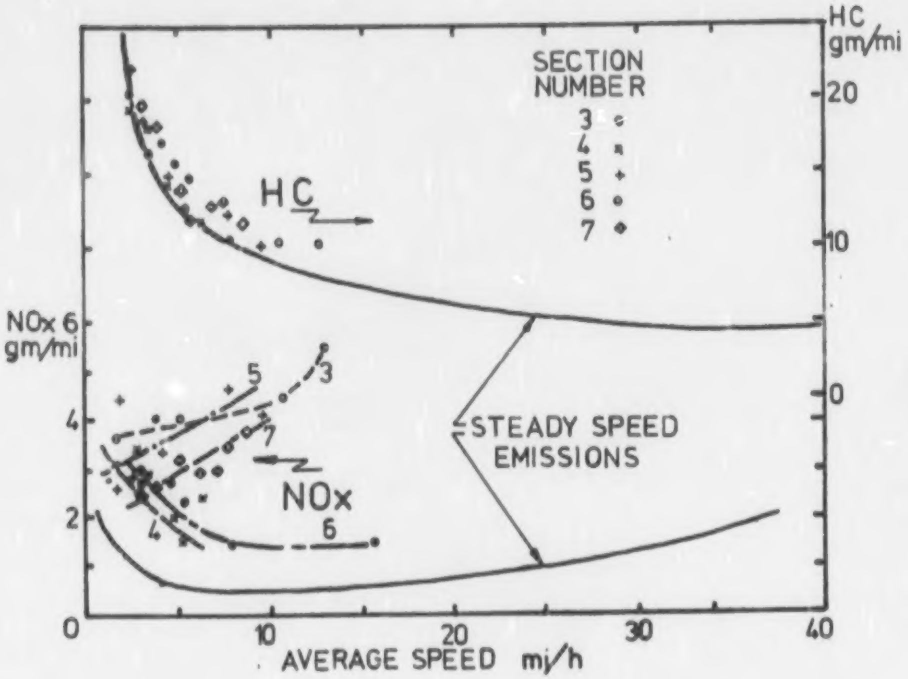

Figure 9. NO_x and HC emissions rates from average vehicle in saturated traffic for CBD sections. Also shown are steady-speed emissions.

The cause of the NO_x reduction achieved on different sections may be seen in Figure 10, where the reduced speed range of Section 6 compared to 3 can be seen from the cumulative frequency versus speed diagram, and the reduced frequency of high accelerations (and decelerations) can also be observed. These results are not unexpected.

STRATEGIES FOR TRAFFIC CONTROL

Some of the basic strategies for the coordinated control of a large number of intersections include minimum accidents, minimum number of stops, minimum overall delay, and maximum vehicle miles per hour. A typical traffic control system based on the CBD will cover 5% of the road network, 30% of the total city VMT and 75% of traffic signals.

From the above findings we can postulate a simple traffic control policy in which trip times are maintained but not improved. To control NO_x, the acceleration rates and acceleration noise should be minimized. This could be achieved by queueing vehicles in the roadways around the CBD area and then releasing platoons of vehicles from the queue, allowing them to pass through the central area at approximately a steady speed close to the speed limit by sequence control of traffic lights. There is, in many cities, sufficient excess road capacity around the CBD to store vehicles prior to CBD area access under controlled conditions.

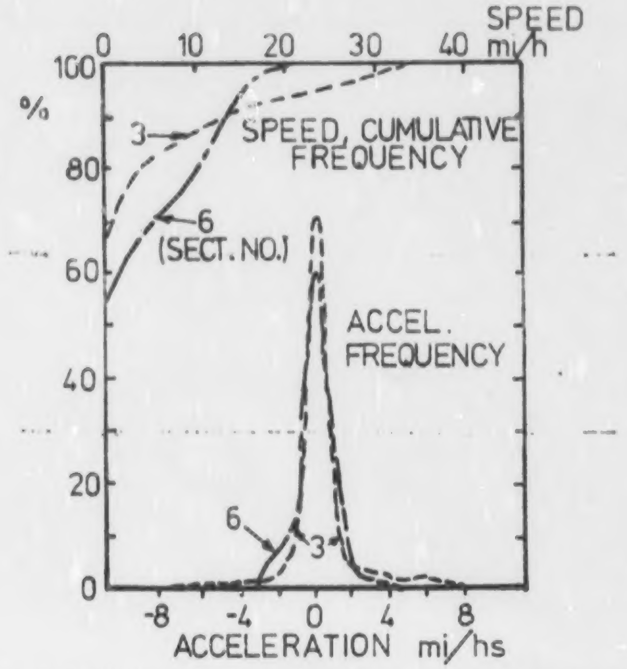

Figure 10. Cumulative frequency versus instantaneous speed and frequency versus acceleration for sections 3 and 6 and saturated traffic flow.

There are two basic methods of control for a coordinated system of traffic lights: the simultaneous and the alternate systems. However, deviations from the fixed time traffic signals can lead to difficulties with traffic streams of unequal volume, which frequently occur in CBD areas. Although not used so far for oxidant precursor control stratagies, these difficulties have not been experienced in Sydney where a comprehensive traffic control system utilizing computer and TV technology has been developed progressively since 1971 (30) and now covers 340 traffic lights. In Melbourne, a computer-controlled system has been investigated. It would be comparatively inexpensive ($1-2M), have a net cost benefit, and improve speeds by 5-10% (31). It should be possible to devise a computer-controlled system which would optimize traffic flow for minimum emissions in the high source CBD areas. This technique has been recognized by the OECD (32).

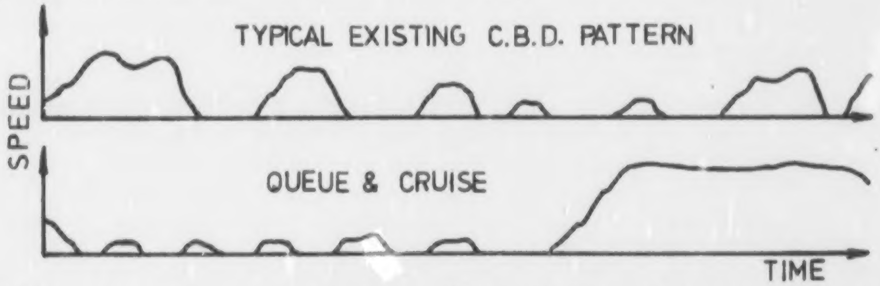

Figure 11. Proposed change to CBD traffic patterns to reduce NO_x emissions source.

The typical resultant changes in driving patterns are depicted in Figure 11 and the changes in HC and NO_x are given in Table 4. The 50% reduction applies to the section overall; the reduction in the CBD component will be much greater (66% NO_x and 48% HC).

TABLE 4 : EFFECT OF TRAFFIC PATTERN MODIFICATION ON PRECURSOR EMISSIONS

Section Length ml	ml/h	Queue* Length ml	HC Before gm/ml	HC After gm/ml	HC Reduc. %	NO_x Before gm/ml	NO_x After gm/ml	NO_x Reduc. %
2	8	0.5	11.6	10.3	11	3.8	1.87	50

* 2 lanes per lane of C.B.D. flow.

CONCLUSIONS

A vehicle emissions model has been developed which has been used in conjunction with a study of traffic patterns for four city driving types. The driving patterns are most closely explained by the halts per mile and average speed. Hydrocarbon emissions are closely related to average speed. The influence of acceleration/deceleration rates and frequency is a second order effect which can cause a ±30% additional variation in HC emissions. The dependence of NO_x on speed is small and acceleration variations can cause ±70% variation in emissions at the same speed. To establish NO_x inventories, it is necessary to take into account the dependence on acceleration. This is the subject of continuing research using the acceleration noise approach.

There is a strong relationship between traffic density per unit area and the radial distance from the CBD. The highest concentratration of precursors occur at the city centre and fall to about half the maximum value at a two-mile radius. Some 45 percent of the total city traffic emission originate within a four-mile radius. For uncontrolled vehicles the HC/NO_x ratio is 2.7-3.1 over the whole city.

There are significant differences in the acceleration rates between our Melbourne measurements and the LA (EPA) City Cycle. The average speed is also lower, which could effect future vehicle emission control policy in a city with a different traffic driving cycle than the LA 4 cycle.

Traffic management as a primary NO_x control strategy appears practical. Steady-state driving would reduce NO_x emission by 90%. Reductions of 60% have been achieved in the CBD area where traffic speeds are very low--8-12 ml/h. A queue and cruise system involving simple traffic signalization could accomplish this.

Greater reductions in oxidant precursor emissions should be achieved by computerized optimization of traffic flow, which would tend to increase average speeds, smooth flow, and reduce acceleration rates and acceleration noise. Hydrocarbon emission from an individual vehicle would fall 20% by increasing the average speed from 12 to 20 mph.

The control of photochemical oxidant precursors by traffic management is attractive because of the potential community savings in reduced pollution, coupled with reduced direct energy consumption, increased safety, and reduced travel time. This has been recognized by the OECD. Further reductions in model vehicle emission standards would be borne by the whole motoring community irrespective of local air quality needs.

The results of this work are directly applicable to the photochemical model builders.

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CONTROL OF VEHICLE REFUELING EMISSIONS

A. M. HOCHHAUSER AND L. S. BERNSTEIN*

ABSTRACT

A four-day test of the Exxon Company U.S.A. manifolded vapor balance system for the control of vehicle refueling emissions was carried out at a service station in Linden, New Jersey. Vapor recovery nozzles were used on all six active dispensers at the stations. Four of the six dispensers were instrumented to carry out the leak-rate and baseline methods of measuring refueling emissions.

With the combined leak-rate-baseline method, we obtained valid emissions measurements on 458 of the 764 cars on which testing was attempted. On 77 cars, no seal was obtained at the nozzle-fillneck interface; 8 of these cars could be fueled only with hand-held operation. On an additional 14 cars, a seal was obtained, but hand-held operation was required. Forty-nine tests had to be discarded because of incomplete data, and on 179 cars a seal was obtained, but emission measurements could not be made because the driver refused to cooperate with our test.

The major reasons for failure to make a seal at the nozzle-fillneck interface were: obstruction by the license plate or bumper, no inner lip on the fillneck, too sharp a bend in the fillneck, and cars on which the technician was unaware that a seal had not been made. We estimate that approximately two-thirds of the cars on which a seal was not made could have been sealed if a no seal-no flow nozzle was used.

The baseline portion of the test procedure indicated average uncontrolled emissions from the vehicle sample of 4.15 g/gal, in good agreement with other studies. Without the no seal-no flow nozzle, we measured 87% emissions control if all cars were considered, and 88% control if cars requiring hand-held operation were excluded according to the Environmental Protection Agency's proposed rules. We estimate that use of a no seal-no flow nozzle would have provided 93% control of these emissions.

INTRODUCTION

VEHICLE REFUELING EMISSIONS

When the fuel tank of an automobile is partially filled with gasoline,

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the vapor space above the liquid contains a mixture of hydrocarbons (HC) and air. During the refueling operation, as liquid is pumped into the tank, vapor is forced out in approximately equal volumes. These vapors, referred to as vehicle refueling emissions, have a magnitude of approximately 3 to 5 g HC/gal. of dispensed fuel. Exact emission rate is a complex function of the temperatures and Reid Vapor Pressures (RVP) of the dispensed fuel and fuel in the vehicle tank. Earlier work(1) at Exxon Research showed that the ratio of vapor generated to liquid dispensed could be calculated:

$$\frac{V}{L} = 1 + (\Delta T)(1.02 \times 10^{-2} - 2.06 \times 10^{-4} T_t - 8.88 \times 10^{-4}\ \mathrm{RVP})$$

where V = Volume of vapor generated,

L = Volume of liquid dispensed,

$\Delta T = T_t - T_d$, °F,

T_t = Tank fuel temperature, °F,

T_d = Dispensed fuel temperature, °F,

RVP = Reid Vapor Pressure of the fuel.

Since engine heat generated during vehicle operation usually results in fuel tank temperatures above dispensed fuel temperature, the volume of vapor generated will usually be smaller than the volume of liquid dispensed, a situation referred to as vapor shrinkage. If dispensed fuel temperature is higher than tank fuel temperature, the volume of vapor will be greater than the volume of liquid dispensed, a situation referred to as vapor growth.

VAPOR BALANCE SYSTEMS FOR THE CONTROL OF VEHICLE REFUELING EMISSIONS

Vapor balance systems (Figure 1) are the simplest, most cost effective method of controlling vehicle refueling emissions. They work by routing the vapors displaced from the vehicle tank through a vapor return line to the underground tank from which the fuel was pumped. These systems require a tight seal at the nozzle-vehicle tank interface. If a tight seal is maintained, and there is no vapor growth, vapor balance systems should give zero emissions. In cases of vapor growth, excess vapor volume can be vented through the normal underground tank vent.

There are two types of vapor balance systems, manifolded and unmanifolded systems. In unmanifolded systems, the vapor from each dispenser is routed back to the underground tank from which its fuel was dispensed. In manifolded systems, vapors from all dispensers at a service station are manifolded before being routed to the underground tanks, which are also manifolded. Manifolded systems have the ability to balance vapor growth and vapor shrinkage when they occur simultaneously.

MEASUREMENT OF VEHICLE REFUELING EMISSIONS

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MEASUREMENT OF VEHICLE REFUELING EMISSIONS

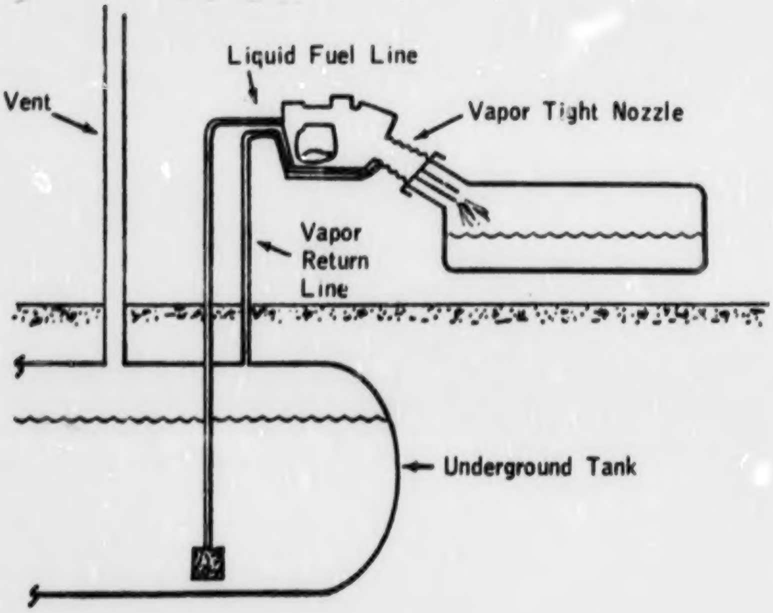

Figure 1. Vapor balance system.

There are two sources of potential emissions from vapor balance systems: emissions from the underground tank vent, and leaks at the nozzle-fillneck interface. Measurement of emissions at the tank vent is conceptually simple. The emitted hydrocarbon can be collected on a carbon trap, or the volume and HC concentration of vent emissions can be determined. Measurement of leaks at the nozzle-fillneck interface is more difficult because the leak rate is a sensitive function of the pressure drop in the system. Increasing or decreasing pressure drop will change the vapor flow characteristics of the system and may lead to erroneous answers. Three general approaches to measuring leaks from vapor balance systems have been developed: the leak-rate method(2), the baseline method(3), and the vacuum collecting tube method(4).

The leak-rate method involves calibration of the leak actually occurring during a refueling operation for each vehicle. The procedure involves two steps: calibration and measurement.

- Calibration: The dispensing nozzle is latched in place, and using appropriate valving, HC vapor is pumped into the tank at low pressure less than 1" of H_2O. If flow can be maintained, a leak is present and HC vapor is pumped into the tank at three different pressures, allowing the "leak-rate" curve of volume of leak (in cfm) vs. ΔP (in inches of H_2O) to be determined.

- Measurement: During refueling, the pressure at the nozzle-fillneck interface and the concentration of HC in the vapor return line are recorded. The volume of leak is calculated from the curve developed in the calibration step. Assuming that the concentration of HC escaping through the leak is the same as the concentration of HC in the vapor return line, refueling emissions can be calculated as follows:

$$\text{Emissions, g/gal} = \frac{\text{Volume of leak, ft}^3\text{/min x HC concentration, g/ft}^3}{\text{Fuel dispensing rate, gal/min}}$$

The major limitation of the leak-rate method is that it cannot be used when no seal is made at the nozzle-fillneck interface and gives poor results when large leaks are present.

The baseline method determines emissions as the difference between potential emissions and the amount of vapor recovered. Prior to refueling, the temperature of the fuel in the vehicle tank (T_t) is measured. The average temperature of the dispensed fuel (T_d) is determined during refueling. The difference between the two temperatures is defined as ΔT (T_t-T_d). During refueling, the amount of vapor returned is measured with a gas meter and HC analyzer. An explosimeter or leak test is used to determine whether leaks are occurring at the nozzle-fillneck interface. Those vehicles for which no leaks are detected are used as the "baseline" population. The amount of vapor returned with these cars is plotted against ΔT, and the resulting correlation is taken to represent the amount of vapor which would result if no control were used. The emissions for cars in which leaks are found are calculated as the difference between estimated uncontrolled emissions (from the correlation with ΔT) and the measured amount of vapor returned.

The vacuum collecting tube method is currently under development by the Environmental Protection Agency. This procedure uses an open-ended sleeve that fits loosely around the nozzle-fillneck interface. Air and any hydrocarbon leaking from the interface are drawn through a series of perforations on the inner face of the sleeve at a rate of 2-5 cfm. The volume and hydrocarbon content of the material collected by the sleeve are determined and used to calculate emission rate. When fully developed, this method should provide a simple, more direct approach to measurement of these emissions. We recommend that EPA make every effort to replace the more complex methods described above with this easier method.

EXPERIMENTAL

Vehicle refueling emission control technology is currently in a state of flux. New hardware and new test procedures are being introduced at a rapid rate. We therefore view the test described in this paper as indicative of the state-of-the-art when the experiment was designed, rather than a definitive measure of the capabilities of the vapor balance system for control of refueling emissions.

The test was carried out using the Exxon Company U.S.A. manifolded vapor balance system(5) at the Research Exxon Service Station located at the southwest corner of the intersection of U.S. 1 and Park Avenue in Linden, New Jersey. This station was chosen because of its high volume (>100,000 gal/month) and its proximity to the Exxon Research Center and its facilities. Emission measurements were made using both the leak-rate and baseline methods. We learned of EPA's efforts to develop the vacuum collecting tube method after the completion of the test. Vent emissions were collected in a carbon trap and determined by weight.

The test was run for four consecutive days in April, 1976, from 6:00 a.m. to 10:00 p.m. Refueling, all test procedures, and data logging were carried out by Exxon Research technicians. The service station normally operates six active dispensers, two each on leaded regular, leaded premium, and unleaded gasoline. All six dispensers were equipped with vapor recovery nozzles, but only four of the six dispensers were equipped with the instrumentation necessary for carrying out emission measurements. One of the leaded premium and one of the unleaded regular dispensers were left uninstrumented because of manpower limitations. The test as designed required 12 people on each of two 8 hr. shifts, a total of 24 people.

Measurements taken included:

- Vehicle tank fuel, dispensed fuel, and returned vapor temperatures;
- Pressure at the nozzle-fillneck interface and ambient pressure;
- Volume of: (a) vapor flowing during the leak-rate calibration, (b) the vapor returned to the underground tank, and (c) the fuel dispensed; and
- HC concentration of the returned vapor.

We also recorded the date and time of the test, vehicle identification information, the number of miles driven since the start of the driver's trip, whether there was spill or spitback, and whether the fuel tank was partially or totally fueled.

The measurement of the volume of vapor returned to the underground tank necessitated placing a dry test meter in the vapor return line. This raised the pressure drop between the nozzle and the underground tank from 0.03 to 0.14 inches of H_2O. The results obtained by the leak-rate method were corrected for the increase in pressure drop created by the dry test meter.

RESULTS

LEAK-RATE METHOD

Over the course of the four-day test, measurements were attempted on 764 light duty vehicles refueled at the station. These vehicles can be broken up into the following categories for the leak-rate portion of the test procedure.

- No leak - A total of 242 cars were determined to have no leak, based on the fact that they showed vapor tight seals during the leak-rate calibration and a measurable amount of vapor was returned to the underground tank.

- Measurable leaks - There were 203 cars on which the nozzle did not form a tight seal and for which a leak was measured by the leak-rate procedure.

- Incomplete data - Data on 49 cars had to be discarded for reasons including instrument failure and technician error.

- Nc fit - There were 77 cars on which no seal was made at the fillneck and no vapor returned to the underground tank. This category included tests in which the vehicle's driver refused to participate in the test, but in which the technician noted that a seal was not made.

- No latch - There were 14 cars on which refueling could be accomplished only by hand-holding the nozzle, but on which some vapor was returned to the underground tank. Data obtained on these cars could not be analyzed by the leak-rate method, but could be analyzed by the baseline method.

- Refusals - 179 drovers refused to participate in the test.

Emissions from the 445 no-leak and measurable-leak cars averaged 0.23 g/gal before correction for the increased pressure drop caused by the dry test meter. Correction for this increased pressure reduced emission to 0.15 g/gal. The corrected figure will be used for all further discussion of the data.

The 77 no-fit cars could not be fit for the following reasons.

- 21 cars had no inner lip on the fillneck. The vapor recovery nozzle makes a seal by latching a ferrule under the lip of the fillneck and forcing the face of a rubber boot against the face of the fillneck. With no inner lip, no seal can be made. All of the cars in this category were improts manufactured by Nissan, Fiat, Peugeot, BLMC, and Volkswagen.

- 10 cars had a sharp 90° bend in the fillneck which prevented the nozzle tip from entering far enough to engage the latch ferrule. Ford vans were the most common vehicle with this problem, but the problem was also encountered with a Dodge van, and cars manufactured by Fiat and Toyo Kogyo.

- 34 cars had obstructions from either the bumper or the license plate preventing the nozzle from properly sealing. This category contained a wide variety of U.S. and imported cars.

- 10 cars had no apparent leak during the leak-rate calibration but were classified as no-fit when it was discovered that no vapor was returned to the underground tank.

- 1 car was reported to have too narrow a fillneck to be sealed by the nozzle.

- 1 car had severe rear-end damage.

Hand-held operation was required on 8 of the 77 no-fit cars.

BASELINE METHOD

Of the 242 no-leak tests reported in the leak-rate method, 125 could be used for the baseline regression equation. The rest of the tests had missing data -- usually initial tank temperature-- which is an extremely difficult measurement to make. It was possible to determine baseline emissions on 142 of the 343 refuelings on which vapor tight seals were not obtained. Here again the data most often missing was initial tank temperature. No-fit and no-latch refuelings were included in the 343 cars with leaks.

The baseline regression was determined to be:

$$\text{g HC/gal} = 4.04 - 0.046\ \Delta T$$

This equation explained only 13% of the observed variance and had a standard error of estimate of 1.10, not significantly different from the standard deviation of the raw data, 1.17. Regressions against tank fuel temperature, dispensed fuel temperature, and combinations of these parameters were also attempted, but none were better than the correlation with ΔT.

Average ΔT for all valid tests was -2.2°F with a standard deviation of 9.3°F. Average potential emissions was 4.15 g/gal. Average leak for the 267 no-leak and measurable leak cars on which valid baseline tests were obtained was 0.15 ± 0.21 g/gal. The baseline correlation estimate of emissions should be compared to the uncorrected leak-rate method estimate of emissions, 0.23 g/gal. While it was possible to correct the leak-rate method for the higher pressure drop caused by the dry test meter, there was no way to correct the baseline procedure. Given the high degree of uncertainty around the baseline estimate and the much smaller number of valid tests used in the baseline estimate, the agreement between the two methods was good.

COMBINATION OF LEAK-RATE AND BASELINE METHODS

During the development of our test program we learned that EPA was considering a combined leak-rate/baseline method which would involve using the leak-rate results for small leaks and baseline results for large leaks. We also analyzed the data with this approach using the following criteria.

- If the emissions calculated by the leak-rate method are less than 1.0 g HC/gal, use these emissions.
- If the emissions calculated by the leak-rate test are more than 1.0 g HC/gal, use the baseline emissions.
- For cars in the no-fit or no-latch category, use baseline emissions, if available.
- If leak-rate data are missing, use baseline emissions, and if baseline emissions are missing, use the leak-rate method.

Using these criteria, data were available on 458 cars. Average emissions for these cars were 0.12 g/gal.

UNDERGROUND TANK VENT EMISSIONS

Vent emissions were measured daily and averaged 0.013 g/gal.

TOTAL EMISSIONS USING THE DIFFERENT ESTIMATING METHODS

In estimating total emissions, we are concerned not only with the vehicles for which valid and complete test data were obtained, but with the vehicles in the other categories: incomplete data, no-fit, no-latch, and refusals. It should be remembered that vehicles on which a tight fit could not be made were considered no-fits, whether or not the driver agreed to participate in the test. Total emissions are the sum of emissions at the nozzle-filltank interface and the 0.013 g/gal emitted at the vent.

For the leak-rate method, the best estimate of the emissions from the 673 cars in the no-leak, measurable-leak, incomplete data, and refusal categories, are the emissions from the 445 cars on which valid and complete data were obtained. Total emissions for these cars averaged 0.16 g/gal. The best estimate for the 14 no-latch cars was also determined in the baseline procedure and found to be 0.58 g/gal. The average of these values is 0.58 g/gal. If we exclude the 22 vehicles which required hand-held operation (8 of the no-fits and all 14 no-latch vehicles), average emission is estimated as 0.54 g/gal.

For the baseline method, the best estimate of emissions for the 673 cars in the no-leak, measurable-leak, incomplete data, and refusal categories is the 0.16 g/gal found on the 267 cars for which valid and complete data were obtained. The best estimate of emissions for the 77 no-fit vehicles is the 4.23 g/gal found on the six no-fit cars for which valid baseline estimates were obtained. The best estimate of emissions for the 14 no-latch cars is the 0.58 g/gal found on the three no-latch cars for which valid baseline tests were conducted. The average for the baseline procedure is 0.58 g/gal. Excluding hand-held operation from this calculation yields an average of 0.54 g/gal.

For the combination method, the best estimate of emissions for the 673 cars in the no-leak, measurable-leak, incomplete data, and refusal categories is the 0.13 g/gal found for the 458 cars on which valid and complete test data were available. For the no-fit and no-latch cars, the baseline values of 4.23 and 0.58 g/gal were used. This results in an average of 0.55 g/gal with hand-held operation and 0.51 g/gal without hand-held operation.

The bulk of the emissions in all cases comes from the 77 no-fit vehicles. Since the estimates of emissions from these vehicles (4.15 vs. 4.22 g/gal) were very similar, it is not surprising that the totals estimated by the three different methods agree so well.

If we assume potential emissions of 4.15 g/gal, overall system efficiency can be calculated to be 86.1-86.8% if hand-held refuelings are included, and 87.0-87.7% if hand-held operations are excluded. These values are quite close to the 90% recovery envisioned in EPA's regulations.

A comparison of the results obtained with the various test methods is contained in Table 1. We have also included an estimate of the potential control obtainable with a no seal-no flow nozzle, that is, a nozzle with an interlock that prevents fuel flow unless a seal is made between the nozzle and the fillneck. The basis for this estimate is presented in the next section of the paper.

TABLE 1. TOTAL REFUELING EMISSIONS BY DIFFERENT METHODS

Method	Estimated Total Emissions*	%Control
Leak-Rate	0.58 g/gal	86
Baseline	0.58	86
Combination	0.54	87
Estimated performance with a successful no seal-no flow nozzle	0.29-0.31	93

* Includes hand-held operation.

DISCUSSION

IMPROVED SYSTEM EFFICIENCY

Approximately 2% of the total emissions determined by the combined leak-rate-baseline method were underground tank vent emissions, 25% were from cars on which a seal could be made, and the remaining 72% were from cars on which no seal was made--the no-fit cars. Significant improvements in system efficiency can be made only if the number of no-fits can be substantially reduced.

The analysis of the reasons for no-fits presented above showed that all but two of the 69 cars that were no-fits, and did not require hand-held refueling, fit into one of four categories: 21 had no inner lip on the fillneck, 8 had too sharp a bend in the fillneck, on 7 the vapor line did not open, even though it appeared that a good seal had been made, and on 31 the fillneck was obstructed by either the bumper or the license plate. One of the remaining two cars had rear-end damage, and on the other, the fillneck was too narrow. Below, we will consider the potential improvement in system efficiency which could be afforded by a no seal-no flow nozzle. We estimate that a satisfactory no seal-no flow nozzle could have provided a seal on 44 of the 69 no-fit cars not requiring hand-held operation in this test. We assume that all 21 of the cars with no inner lip on the fillneck, all 7 of the cars on which the vapor return line did not open, and half (15) of the 31 cars on which the license plate or bumper wan an obstruction could have been sealed in this fashion. The cars with too sharp a bend in the fillneck and the remainder of the cars with obstructions would probably not be sealed by the no seal-no flow nozzle. For these cars, some sort of manual override of the no seal-no flow device would have to be provided.

Use of a no seal-no flow nozzle would mean that all of the 69 cars which were previously no-fit cars not requiring hand-held refueling would now require hand-held operation. The cars on which a seal could be made would require hand-held operation to maintain the seal, and the cars on which a seal could not be made would require hand-held operation to override the no-seal-no flow device. If hand-held refuelings were excluded from the data analysis, all of these tests would be dropped from consideration. Using this criterion, the best estimate of total emissions from the remaining cars would be the 0.13 g/gal found for the 458 no-leak and measurable-leak cars, using the combined leak-rate-baseline method. This is equivalent to a system efficiency of 96.8%.

If hand-held refuelings are included in the data analysis, emissions from all 764 cars would have to be considered, and an additional 5 cars would have to be added to the group sealed by the no seal-no flow nozzle. The best estimate of total emissions from the 673 no-leak, measurable-leak, incomplete data, and refusal cars is the 0.13 g/gal found with the combined leak-rate-baseline method. The best estimate of the total emissions on the 49 cars for which the no seal-no flow nozzle would require a seal to be made is between 0.13 and 0.58 g/gal. The lower figure assumes that a seal as good as was made on the cars sealed in this test can be made. The higher figure assumes that the seal will be no better than was made on the no-latch cars. The best estimates of total emissions from the 14 no-latch cars and the 28 remaining no-fit cars are 0.58 and 4.15 g/gal, respectively.

Including hand-held refuelings and assuming total emissions of 0.13 g/gal for cars on which the no seal-no flow nozzle requires a seal to be made results in average emissions of 0.29 g/gal, equivalent to a system efficiency of 93.0%. Assuming the higher value of emissions for these cars, 0.58 g/gal, results in average emissions of 0.31 g/gal, equivalent to a system efficiency of 92.5%. In all of the cases we have considered, a successful no seal-no

For the combination method, the best estimate of emissions for the 673 cars in the no-leak, measurable-leak, incomplete data, and refusal categories is the 0.13 g/gal found for the 458 cars on which valid and complete test data were available. For the no-fit and no-latch cars, the baseline values of 4.23 and 0.58 g/gal were used. This results in an average of 0.55 g/gal with hand-held operation and 0.51 g/gal without hand-held operation.

The bulk of the emissions in all cases comes from the 77 no-fit vehicles. Since the estimates of emissions from these vehicles (4.15 vs. 4.22 g/gal) were very similar, it is not surprising that the totals estimated by the three different methods agree so well.

If we assume potential emissions of 4.15 g/gal, overall system efficiency can be calculated to be 86.1-86.8% if hand-held refuelings are included, and 87.0-87.7% if hand-held operations are excluded. These values are quite close to the 90% recovery envisioned in EPA's regulations.

A comparison of the results obtained with the various test methods is contained in Table 1. We have also included an estimate of the potential control obtainable with a no seal-no flow nozzle, that is, a nozzle with an interlock that prevents fuel flow unless a seal is made between the nozzle and the fillneck. The basis for this estimate is presented in the next section of the paper.

TABLE 1. TOTAL REFUELING EMISSIONS BY DIFFERENT METHODS

Method	Estimated Total Emissions*	%Control
Leak-Rate	0.58 g/gal	86
Baseline	0.58	86
Combination	0.54	87
Estimated performance with a successful no seal-no flow nozzle	0.29-0.31	93

* Includes hand-held operation.

DISCUSSION

IMPROVED SYSTEM EFFICIENCY

Approximately 2% of the total emissions determined by the combined leak-rate-baseline method were underground tank vent emissions, 25% were from cars on which a seal could be made, and the remaining 72% were from cars on which no seal was made--the no-fit cars. Significant improvements in system effiflow nozzle could lower total emissions from the system to below 0.4 g/gal and raise system efficiency to above 90%.

ADDITIONAL WORK

Tests of prototype no seal-no flow nozzles and prototype hybrid vapor recovery systems are planned for the near future.

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SESSION 21

CONTROL OF OXIDANT PRECURSOR EMISSIONS - II

Chairman: R.W. Bilger
University of Sydney, Australia

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NO_x CONTROL TECHNOLOGY FOR STATIONARY SOURCES

G. B. Martin and J. S. Bowen*

ABSTRACT

The Environmental Protection Agency's Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, has an extensive program for control of oxides of nitrogen from stationary combustion sources by modification of equipment design and operating conditions. This paper will briefly describe the levels of emission control that have been achieved on practical combustion equipment. It will then describe several of the Environmental Protection Agency program activities for development of combustion technology capable of significantly enhanced control of oxides of nitrogen.

INTRODUCTION

One of the major classes of pollutants emitted into the atmosphere from man's activity is identified by the term nitrogen oxides (NO_x). Approximately 99 percent of this NO_x is generated from combustion of fuels in a variety of equipment types and the emissions are concentrated in population centers. The evidence indicates that for most equipment types, 95 percent of the NO_x is emitted from the source as nitric oxide (NO) with the balance being nitrogen dioxide (NO_2); however, recent results indicate that for certain sources (e.g., gas turbines) the percentage of NO_2 may be significantly higher. In any event, the total NO_x emitted undergoes a complex scheme of atmospheric photochemical reactions with hydrocarbons (HC) and sulfur oxides (SO_x). These reactions result in the formation of undesirable secondary species, such as ozone (O_3) and nitrates, and in a shift of the residual NO_x toward NO_2. The recognition of the adverse effects of NO_2 and other atmospheric pollutants on human health and welfare led to passage of the Clean Air Act of 1970. As a result of this act the EPA was empowered: (a) to establish a National Ambient Air Quality Standard (NAAQS) for NO_2; (b) to require a 90 percent reduction of NO_x from the automobile; (c) to establish New Source Performance Standards (NSPS) for stationary equipment; and (d) to set up mechanisms to insure compliance.

At the time the Clean Air Act was passed, mobile and stationary sources each contributed approximately 50 percent of the NO_x and the major control strategy was reduction of mobile source emissions by 90 percent to 0.4 gm of NO_2 per mile (0.25 mg of NO_2 per meter). NSPS were provided to reduce growth of NO_x emissions from stationary sources. Since that time a number of factors have emerged which appear to require some modification of this

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approach to NO_x control. First, development of economic control technology to meet the automobile emission goal has proved elusive. Second, the energy crisis has provided strong pressure for use of coal in utility boilers with an attendant increase in NO_x emissions. These factors and others have resulted in a greater emphasis on NO_x control for stationary sources and in a recommendation for a Maximum Stationary Source Technology (MSST) program for control technology development (1).

There are a number of potential approaches to control of NO_x from stationary combustion sources:

(1) Combustion modification, which is based on alteration of combustion conditions to minimize formation of NO_x, is potentially applicable to all types of combustion sources both new and existing.

(2) Flue gas treatment, which involves an add-on device to remove the NO_x from the flue gas, is currently envisioned as a method to supplement combustion modification where a high degree of control is required.

(3) Advanced alternate fuels and combustion processes may have properties leading to inherently low levels of NO_x.

(4) Fluid bed combustion, which is predominantly an SO_x control technique, has favorable characteristics for NO_x reduction, especially with application of combustion modification principles.

The purpose of this paper is to describe the Combustion Modification program as related to items (1) and (3) above. Flue gas treatment and fluid bed combustion programs have been described elsewhere.

BACKGROUND

The combustion modification approach is based on the premise that NO_x can be reduced substantially by alteration of the conditions under which the fuel burns. There are two predominant mechanisms for the formation of NO_x during combustion. Thermal NO_x is formed by fixation of molecular nitrogen from the combustion air through a series of reactions which are exponentially dependent on temperature and slightly dependent on oxygen availability. Fuel NO_x is formed by oxidation of organic nitrogen compounds contained in the fuel through a series of reactions which are relatively independent of temperature and strongly influenced by oxygen availability. For any fuel containing bound nitrogen both mechanisms contribute to the total NO_x formation.

Working from this knowledge of the NO_x formation chemistry, a number of control technology approaches have been formulated. Techniques for control of thermal NO_x are based on reducing the peak temperatures in the combustion zone, and include staged combustion, low excess air, flue gas recirculation, and water injection. Techniques for control of fuel NO_x are based on reduction of oxygen availability in the combustion zone, and include low excess air operation and staged combustion. In addition, pilot scale combustion studies have shown that changes in burner design can also significantly reduce the formation of both thermal and fuel NO_x by aerodynamically influencing local recirculation rates and/or oxygen availability in the flame. The optimum level of control may require a combination of these approaches. Although the control techniques have shown good potential in experimental systems and on some practical equipment, the optimum levels achievable have yet to be established and are the subject of this program. In the application of NO_x control technology to practical equipment, care must be taken to minimize potential adverse side effects. These include: increases of other pollutants, loss of system efficiency, and system operability problems. Based on current information, emissions of other pollutants (e.g., carbon monoxide and other products of incomplete combustion) can be maintained at low levels while achieving significant NO_x reduction by proper system design. Many of the NO_x control techniques, such as low excess air operation, even offer potential for increases of system efficiency. Based on limited experience with long term service it appears that operability problems, including fireside corrosion, can be avoided by proper design.

COMBUSTION MODIFICATION PROGRAM

The NO_x control technology development program was initiated in 1969 at the conclusion of a systems study conducted under contract by Esso Research and Engineering (2). The system study provided an emission inventory by source category and fuel usage; in addition, it reviewed the available technology and development potential of various control approaches and concluded that the combustion modification techniques to reduce NO_x formation offered the most cost effective potential. Based on this study and the available resources, a Combustion Modification R&D program was structured to develop and apply control technology for the equipment type and fuel combinations which constituted the major stationary sources of NO_x. These major sources are shown in Table 1 based on a recent updated emission inventory (3). In addition, the NO_x control technology developed was to be capable of minimizing undesirable side effects of the technology, and maintaining or improving process energy efficiency. Ongoing developments in the private sector (e.g., gas- and oil-fired utility boilers) were considered to insure complementary activity where appropriate and to avoid duplication where significant private effort exists. Details of the program have been documented in detail in two recent papers (4, 5).

This basic philosophy has been followed, although in the intervening years the program emphasis has been expanded and shifted to account for recent trends. As an example, in response to the recent increase in emphasis on stationary source NO_x control and the Clean Air Act requirement for demonstrated technology as the basis for any NSPS, Industrial Environmental Research Laboratory-Research Triangle Park (IERL-RTP) has Aerotherm working under contract to establish the requirements for a Maximum Stationary Source Technology (MSST) program. The inventory identified 137 combinations of equipment type and fuel that account for the stationary source NO_x of which 38 contribute 90 percent (3). While this appears to be a formidable number of combinations, there are many common features of the systems which allow general application of the technology and, therefore, a manageable development effort. A report containing the final recommended program and funding levels is currently in preparation.

TABLE 1. SUMMARY OF TOTAL NO_x EMISSIONS FROM FUEL USER SOURCES (1972)

Sector	NO_x Production (percent of total)			Totals by Sector (percent of total)	Cumulative Percentage
	Gas	Coal	Oil		
1. Utility Boilers	9.55	32.47	6.58	48.61	48.61
2. IC Engines					
Reciprocating	16.06	--	2.71	18.77	67.38
Gas Turbines	1.47	--	1.02	2.49	69.87
3. Industrial Boilers	4.24	4.41	9.41	18.07	87.94
4. Commercial/Residential Heating	2.84	0.25	4.00	7.09	95.03
5. Process Heating	1.59	0.47	1.28	3.35	98.38
6. Non-Combustion	--	--	--	1.28	99.66
7. Incineration	--	--	--	0.35	100
Totals by Fuel	35.75	37.61	25.01	100	

(a) Total Emissions = 11.665×10^6 tons/yr (10.582×10^9 kg/yr)

The general program approach involves five types of activities:

- Field testing provides accurate emission information on the source class as normally operated in the field and evaluation of control possible through changes in operating conditions only.
- Process research and development evaluates the potential for minor hardware changes for increased level of control by retrofit and, thereby, provides guidance for application of existing technology to new designs.
- Fuels research and development provides general development of various techniques for controlling NO_x from each fuel type independent of equipment type, optimization of the technology for each fuel, and general guidance for application of the optimum technology to a variety of practical systems.
- Fundamental studies of combustion chemistry and aerodynamics promote understanding of the combustion phenomena responsible for pollutant formation and, thereby, guide development and optimization of new technology.
- Environmental assessment documents the impact of the NO_x control technology on total system performance and emissions to air, water and land.

PROGRAM STATUS

The results of the program to date fall into two general areas: (a) development and application of control technology to specific source categories, and (b) generation of technological approaches of potential applicability to a wide range of sources.

The development and application of technology for specific practical equipment has concentrated on the major heat and steam generating sources of NO_x. These are utility, industrial and commercial boilers, and residential heaters. The significant results to date can be summarized as follows:

(1) Utility boiler field testing has established reliable emission factors for boilers fired with coal, oil and natural gas, and has indicated that significant levels of control are achievable through modification of operating conditions with the specific level of control dependent on fuel type and boiler design (6). In addition, it has been shown that by minor hardware modifications to apply staged combustion, NO_x levels can be reduced by 30-40 percent for coal fired boilers already operating at or slightly above the NSPS for that type of equipment. Efficiency and fireside corrosion results are encouraging but show that more attention to these areas is necessary.

(2) Industrial and commercial boiler field testing has also established reliable emission factors for a variety of fuels; however, it has

indicated that the relatively simple designs of these boilers make them less amenable to NO_x control by possible changes in operating conditions. The development and application studies, in which the emphasis has been on small package type boiler fired with heavy oil and natural gas, have shown the potential for NO_x reductions of up to 50 percent for the heavy oil by application of staged combustion and over 60 percent for gas with flue gas recirculation (7, 8).

(3) Residential furnace emission factors have also been established; however, changes in operating conditions, which consist of tuning, generally increase NO_x slightly (9). The development effort has produced an oil burner head design capable of reducing NO_x relative to conventional practice. Further development of an integrated furnace to achieve a 50 to 75 percent reduction of NO_x coupled with an efficiency increase is nearing completion (10). Field application will be evaluated in the near future.

The development of advanced technological approaches consists of investigations in three general areas: optimization of burner design and other techniques to establish minimum NO_x emissions achievable for conventional fuels and system design; assessment of alternate fuels and equipment design approaches for ultimate control potential through system redesign; and fundamental studies to provide understanding and guidance for the first two areas. Selected significant results in each area are given below:

(1) Major effort for development of optimized technology has concentrated in the area of burner design alteration to give low NO_x and efficient combustion conditions. Critical parameters have been established for natural gas and pulverized coal and progress has been made for residual oil. Possibly the most significant result was the establishment of conditions capable of reducing NO_x from a single pulverized coal burner from approximately 900 ppm to approximately 150 ppm (11).

(2) Advanced concept studies, which have been initiated, include alternate fuel combustion and catalytic combustion. The only alternate fuel evaluated to date is methanol, which appears to have favorable combustion and emission characteristics (12).

(3) The fundamental studies have produced kinetic rate information for gas phase and fuel decomposition reactions, as well as basic aerodynamic mixing information for turbulent diffusion flames. This information provides input for development of engineering design models for application and optimization of the technology (13, 14).

PROGRAM DIRECION AND GOALS

The program direction and goals are strongly dependent on both the level of funding and the duration of the program. Table 2 shows approximate current emission levels for uncontrolled sources and the estimated level of NO_x control achievable in 1980 and 1985 for the 10 year MSST. The near term goals should be possible with hardware changes (e.g., burner design for conventional boiler design, while the long term goals may depend on significant system redesign and/or application of advanced concepts. Although the technology to achieve these levels can almost certainly be developed by the year shown, the demonstration in practical equipment will depend on equipment lead time and other factors, particularly for the larger systems (e.g., utility boilers). For less than a maximum program, lower priority sources will be dropped from consideration. Based on the current projected funding and a program duration of 5 years, the probable achievable technology and demonstration goals are indicated by notation on 1980 goals in Table 2. The other 1980 goals are achievable, but are not currently under intensive development. This technology also has the potential for application to current equipment with a lower probable degree of control. The 1985 goals would be outgrowths of the technology with significant system redesign (i.e., combustion and heat exchanger design matching) and/or utilization of advanced technology currently under development (e.g., catalytic combustion).

To illustrate the total approach, consider the overall development history for wall-fired coal burning utility boilers shown in Table 3. Given the significant decrease available by relatively minor changes in hardware and operating conditions coupled with the low level achievable on a small coal burner at the International Flame Research Foundation, achievement of 200 ppm in a field operating utility boiler by application of an optimum burner can be projected with high probability.

A second example can be taken for residential heating systems to illustrate not only NO_x control with no increase of carbonaceous emissions, but also improved efficiency. The initial development was an optimum oil burner head suitable for retrofit to at least 50 percent of existing residential furnaces with an NO_x reduction of 20 to 50 percent and no loss in efficiency. This burner head was then matched to a combustion chamber design with the goal of a 75 percent NO_x reduction and improved furnace efficiency. The performance of a prototype of this integrated furnace is shown in Figure 1 and is compared to the performance of both the overall furnace population and the unmodified stock furnace. It can be seen that the NO_x goal was almost achieved at an operating excess air level that represents an efficiency gain. Carbonaceous emissions were maintained at low levels (10).

Finally, the exploration of advanced concepts and utilization of alternate fuels may provide the basis for longer term (1985) technology to virtually eliminate NO_x emissions from some sources. For bound-nitrogen-free fossil and coal-derived fuels, catalytic combustion concepts may allow NO_x to be controlled to the level of 10 ppm or less. Control of NO_x from nitrogen-containing alternate fuels appears somewhat more complex; however, it appears that this combustion technology should also be applicable (15).

CONCLUSIONS

The developing combustion modification technology can form the basis for significant New Source Performance Standards in the future for several stationary combustion systems. Implementation of a 10-year MSST strategy can significantly broaden the degree of control and demonstrated source application achievable with the technology. It also appears that any adverse impacts of NO_x control on cost, energy efficiency, and other emission can be minimized or eliminated by proper technology application.

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TABLE 2. TECHNOLOGY DEVELOPMENT RESEARCH GOALS--AVERAGE NO_x (ppm @ 3% O_2)

Source	Current Technology	1980 Goal	1985 Goal
Utility			
Gas	150(a)	100	50
Oil	225(a)	150	90
Coal	550(a)	200(c)	100
Industrial			
Gas	150	80	50
Residual oil	325	125	90
Coal	450	150(c)	100
Commercial			
Gas	100	50	30
Distillate oil	125	70	50
Residual oil	300	100(c)	90
Residential			
Gas	80	25	10
Distillate oil	115	35(c)	10
Reciprocating Engines			
Spark ignition--gas	3000	1200(d)	400
Compression ignition--oil	2500	1200(d)	800
Gas Turbines			
Gas	400[150(b)]	75(d)	25
Oil	600[225(b)]	125(d)	25

(a) Current NSPS
(b) Estimated achievable with wet control technology
(c) Developed and field applied technology
(d) Developed technology from ongoing EPA program

TABLE 3. EXAMPLE CONTROL DEVELOPMENT HISTORY
WALL FIRED, COAL BURNING UTILITY BOILERS

Event	NO_x Level (ppm @ 3% O_2)	Year Achieved	
		Actual	Projected
Uncontrolled	900	Pre-1975	
Boiler Operation Change	550	1973	
NSPS	550		1976
Modified System	400	1975	
Small Scale Single Coal Burner--Experimental	150	1972	
Full Scale Optimum Single Coal Burner--Experimental	200		1977
Apply Optimum Burner	200		1980

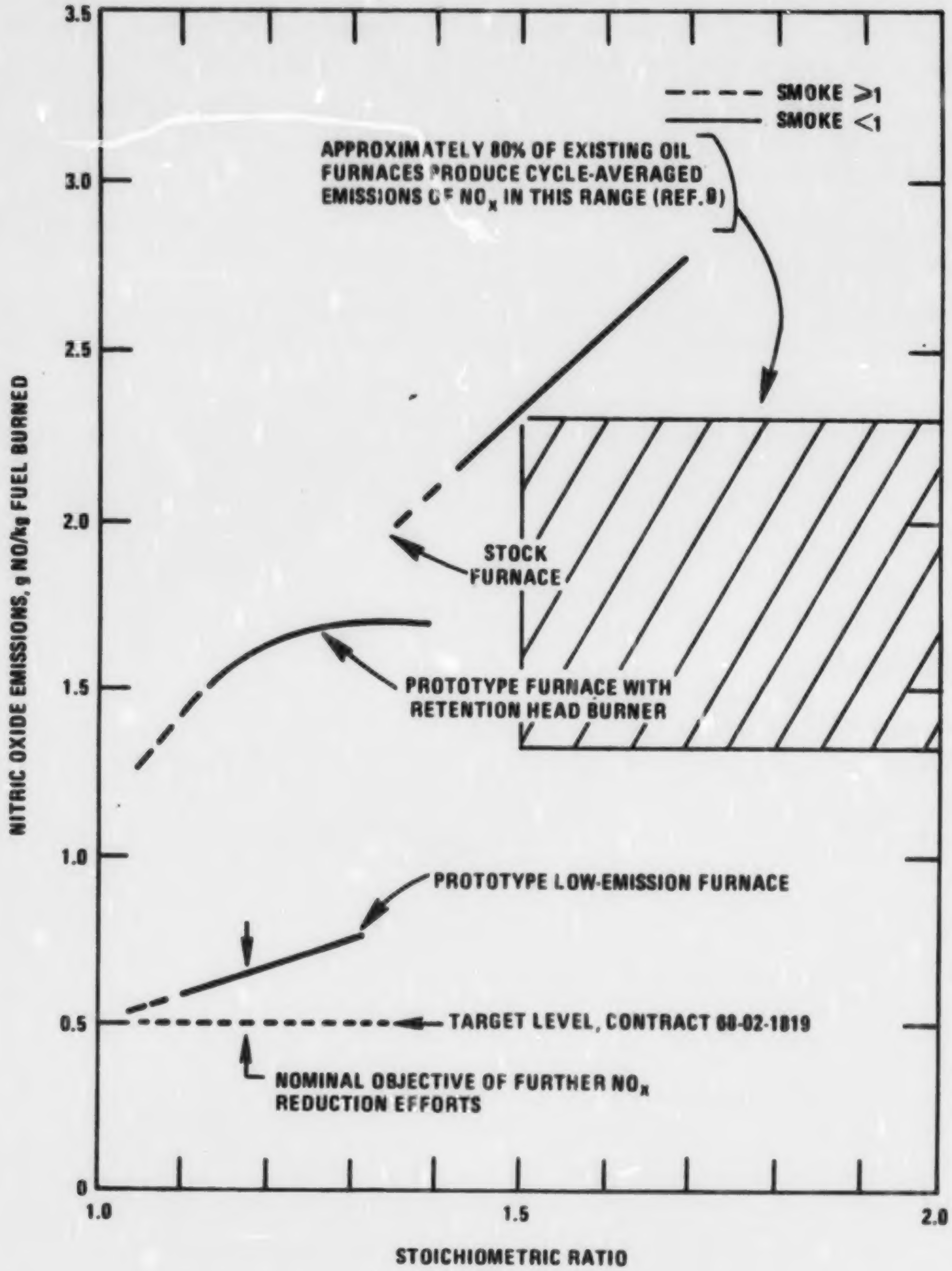

Figure 1. Cycle-averaged flue gas NO concentrations, comparison of the prototype optimum furnace with other existing units.

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EMISSION ESTIMATES OF NO_2 AND ORGANIC COMPOUNDS FROM COAL-FIRED FLUIDIZED BED COMBUSTION

P. F. Fennelly*

ABSTRACT

Fluidized bed combustion systems operate at significantly lower temperatures than conventional systems (about 900°C versus 1500°C, respectively). Questions have been raised concerning the organic and nitrogen oxides emissions which could result at these lower operating temperatures. Using available data from bench scale or pilot plant fluidized bed combustion experiments and/or simple thermodynamics and empirical correlations with conventional combustion systems, estimates have been made of the concentrations of various compounds in the flue gas. These estimates are probably good to within an order of magnitude.

The results indicate that with respect to formation of photochemical oxidant precursors, no special environmental problems should result from fluidized bed combustion. In fact, this combustion technique offers significant advantages with respect to reductions in nitrogen oxides and sulfur oxides emissions.

INTRODUCTION

A fluidized bed boiler can be simply depicted as an enclosed cavity containing boiler tubes and a bed of granular solids, to which fuel is added. As shown in Figure 1, the solids are supported on a grid, at the bottom of the boiler, through which combustion air is passed at high velocities, typically 2 to 5 feet per second (0.6-1.5 m/s). The solids are held in suspension by the upward flow of the air and a quasi-fluid is created which contains many properties of a liquid. The most important liquid-like property is that the bed material is exceptionally well mixed and flows throughout the system without mechanical agitation.

Fluidized bed coal combustion systems for the production of steam and/or electricity have several advantages over conventional combustion systems.

- High heat transfer coefficients and volumetric heat release rates will reduce the boiler size by one-half to two-thirds or more compared to a conventional unit.

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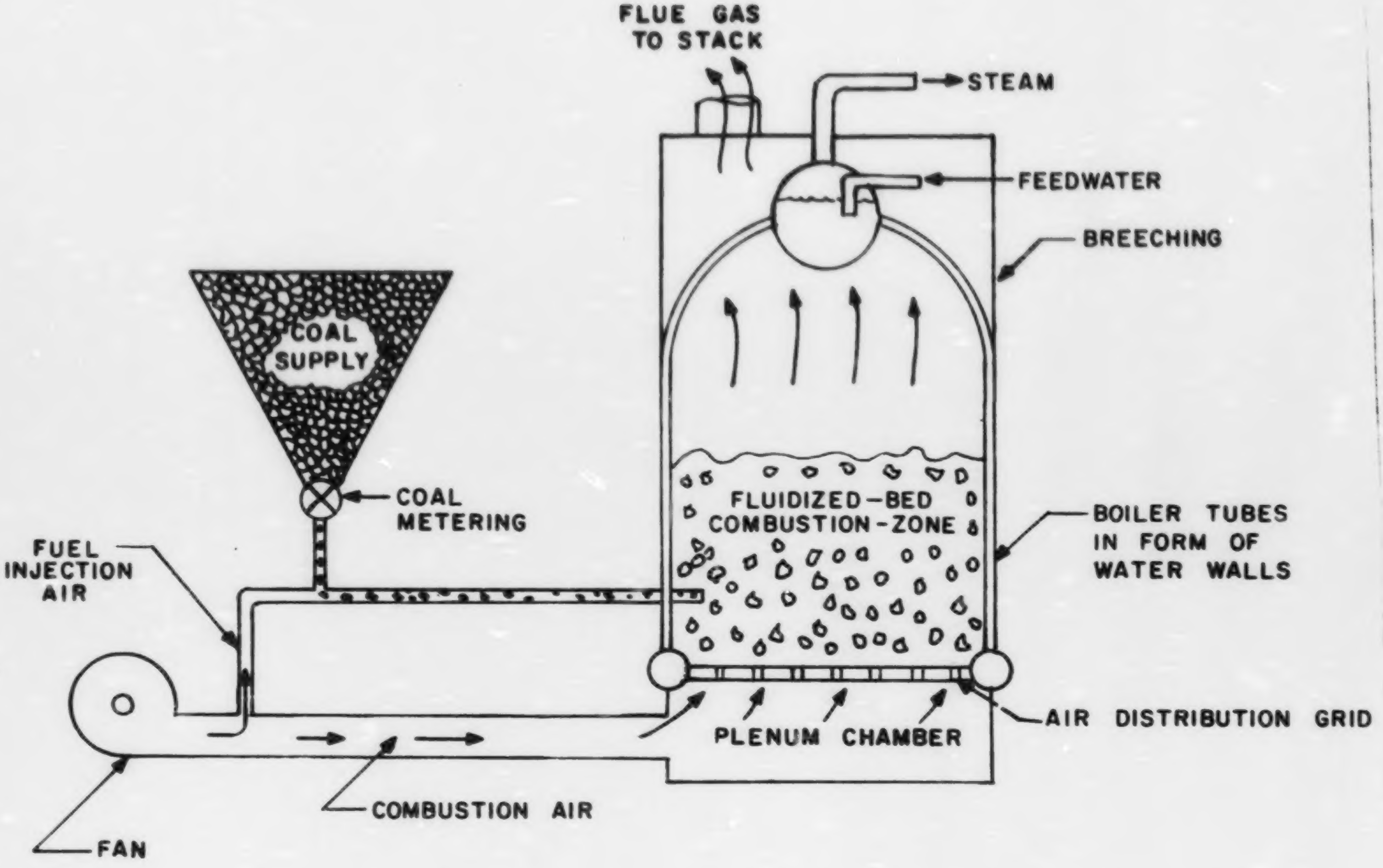

Figure 1. Schematic of fluidized bed boiler (12).

- Capital costs will be reduced due to the size reduction and the potential for shop fabrication instead of field construction.

- The use of limestone as bed material provides a means for in situ sulfur dioxide (SO_2) removal.

- The high heat transfer coefficients permit lower operating temperatures (850 to 950°C) which can potentially decrease nitrogen oxides (NO_x) emission.

Questions have been raised concerning the organic emissions that could result at these lower operating temperatures. Using available data and/or simple thermodynamics and empirical correlations, this paper provides estimates of the concentrations of various compounds that could result from coal-fired fluidized bed combustion (FBC). These estimates are probably good to within an order of magnitude.

STABLE ORGANIC COMPOUNDS

Potential organic pollutants are those compounds which could form from the incomplete combustion of coal. One can view the burning of a coal particle as a sequential process. The particle vaporizes or volatilizes; these volatile compounds can react among themselves in a chemically reducing atmosphere. Next, they react with oxygen within the system in a diffusion flame. After devolatilization is completed, the char continues to burn. In specifying the potential organic compounds which could form, the basic question is what types of chemical species are produced during coal pyrolysis and to what extent will they survive in the reactive environment of a fluidized bed combustor.

The chemical structure of coal can be viewed as a network of interconnected aromatic hydrocarbon compounds (1). Small hydrocarbons (HC) can form directly from cleavage of substituted alkyl groups. Polynuclear aromatic hydrocarbons (PAH) can form directly via bond cleavages in the structural network or they can form via condensation reactions of various HC decomposition products. These condensation reactions even though generally endothermic, based on thermodynamic estimating techniques, at FBC temperatures of 1500°F probably proceed at a significant rate (2,3). Branched or cyclic HC are seldom found as products of coal pyrolysis carried out at similar temperatures (1); hence, only two classes of HC should be of any significance in fluidized bed coal combustion: small HC (i.e., less than three carbon atoms) and PAH. Both could form and survive within the bed at temperatures on the order of 1500°F.

Similar arguments apply to organic nitrogen and sulfur compounds. Species such as pyridine decompose at temperatures of 1000°F to form HCN and small HC (4). Thiophenes and mercaptans can also decompose to form small HC and hydrogen sulfide (H_2S).

CONCENTRATION ESTIMATES OF ORGANIC COMPOUNDS

For a rough estimate of the concentrations at which some of the small HC and reduced sulfur and nitrogen compounds might exist, one can use equilibrium calculations based on free energy minimization. An upper limit can be obtained from calculations performed in conjunction with coal gasification experiments, where highly reducing, fuel-rich conditions exist (5). Even with only 60 per cent stoichiometric oxygen present, the data in Table 1 indicate that HCN, COS, CS_2, etc. are less than 10 parts per million (ppm). Extrapolation of the calculations to typical operating conditions such as 20 percent excess air, where SO_2 and NO_x become the predominant sulfur and nitrogen compounds, indicates that compounds such

TABLE 1. CALCULATED EQUILIBRIUM CONCENTRATION FOR SELECTED SPECIES PRODUCED BY INCOMPLETE COMBUSTION OF COAL[a]

Coal analysis: C-68.5%, H-5.3%, O-8.5%, N-1.4%, S-4.1%

Oxygen present: 59% of stoichiometric requirements

Temperature: 1400°F

Species	Mole fraction
N_2	0.36
CO	0.26
H_2	0.15
H_2O	0.06
CO_2	0.10
CH_4	0.06
H_2S	0.008
COS	0.0005
NH_3	0.0007
C(g), HCN, CS_2	$< 10^{-5}$
C_2H_2, C_2H_4, $(CN)_2$	
S_2, SO_2, SO_3	
N_2, NO_2	

[a] Based on Reference 5

as H_2S, HCN, COS, $(CN)_2$, etc. should be present in concentrations less than 1 ppm. Free energy minimization calculations for the more complicated PAH are impractical. To estimate the concentrations at which these types of compounds might exist in the FBC flue gas, one can use empirical correlations between benzo(a)pyrene and methane (CH_4) concentrations from measurements in conventional coal-fired combustion systems. Figure 2 indicates the variation of total hydrocarbons (as CH_4) as a function of oxygen (O_2) concentration from one set of FBC experiments. Under normal operating conditions, about 3 per cent O_2 in the flue gas (20 per cent excess air), the concentration of HC (as CH_4) is about 100 ppm (volume/volume-V/V) (6). Although emissions can often vary between different fluidized bed systems, 100 ppm provides a convenient reference value. Previous measurements with conventional coal-fired systems indicate that compounds such as benzo(a)pyrene are typically 10^{-5} times less than the concentration of total HC as CH_4(7).

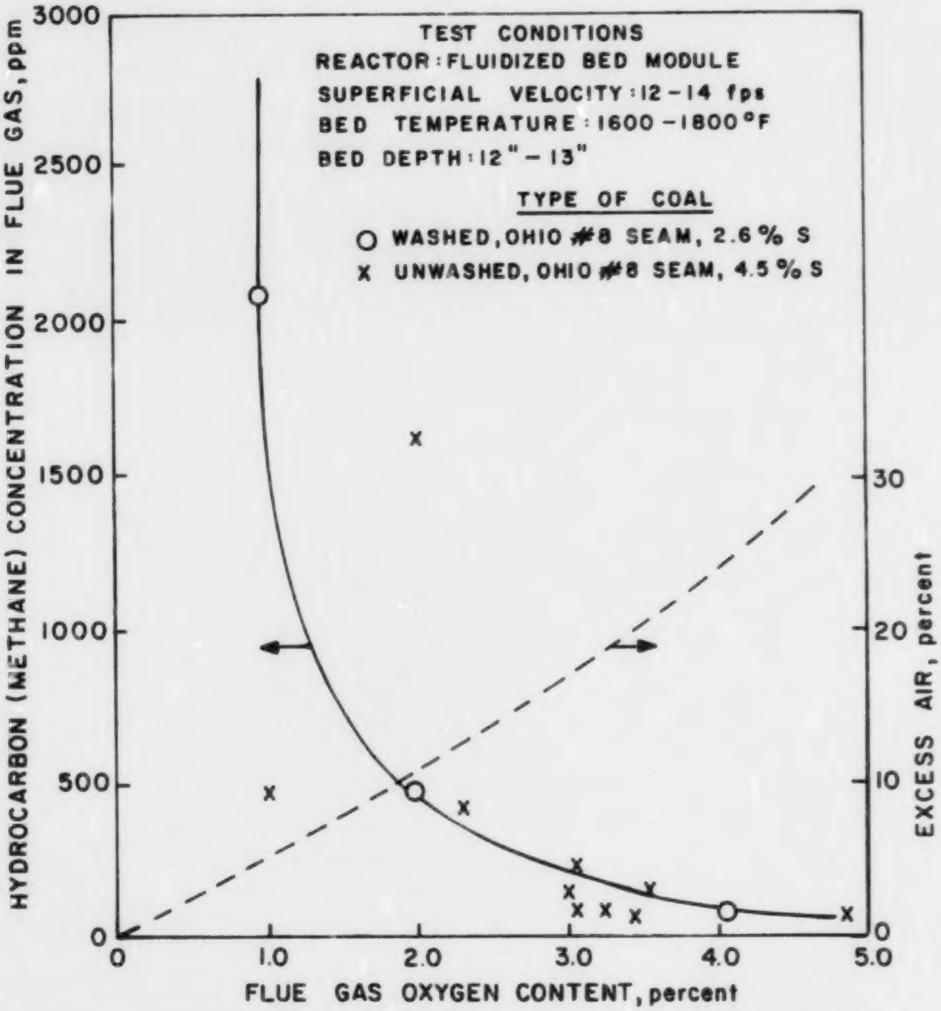

Figure 2. Variation in hydrocarbons concentration with flue gas oxygen content in the FBM (6).

Using our reference value of 100 ppm (CH_4), this implies that in a fluidized bed system, PAH could exist in the flue gas at concentrations (V/V) on the order of 1 part per billion (ppb). Considering that flue gases are eventually diluted by a factor of a thousand when they are emitted from the stack (8), this implies that ambient concentrations of PAH near FBC facilities would be on the order of 1 part per trillion. This corresponds to about 0.6 ng/m^3 which is roughly comparable to the natural background concentration ranges found in rural areas (7). Accordingly, it seems that PAH concentrations should not be high enough to cause problems.

Recently, some conventional coal-fired flue gases have been tested for the presence of polychlorinated biphenyls (PCB) and trace concentrations have been reported (8). Experience in coal combustion and coal pyrolysis indicates that at temperatures similar to that in coal-fired FBC, chlorine (when present) predominatly exists as HCl (1). Accordingly, one would not expect significant concentrations of PCB's in coal-fired FBC. If present at all, they should be in concentrations less than those of the unsubstituted PAH (i.e., <1 ppb (V/V)).

NITROGEN OXIDES EMISSIONS

There is considerably more experimental data available for NO_x emissions in FBC compared with that for organic compounds (9-12). These emissions can vary from system to system and work is underway to summarize the pertinent fluidized bed parameters which influence NO_x emissions. Of special interest are the relative contributions of thermal NO_x and fuel NO_x.

At the temperatures encountered in FBC (1500 to 1600°F), equilibrium calculations based on thermal fixation of atmospheric nitrogen indicate nitric oxide (NO) levels should be 100 to 200 ppm, depending on the amount of O_2 present. In fact, NO levels in most coal-fired fluidized bed experiments conducted at atmospheric pressure are on the order of 300 to 500 ppm (9-12). Two plausible explanations are (1) the excess NO results from hot spots within the bed which are far in excess of the equilibrium temperature, or (2) the higher NO levels result from substantial conversion of the nitrogen in coal. There is some interesting experimental evidence supporting the latter mechanism.

Workers at Argonne Laboratories in a set of experiments on fluidized bed coal combustion substituted argon for the nitrogen in combustion air and found that NO_x levels did not change significantly. In one experiment, the initial NO concentration of 580 ppm did not vary during the argon substitution by more than ± 20 ppm (9,10).

NO_x concentrations in fluidized bed systems, however, can be very apparatus dependent, and significant concentration profiles have been found in some reactors (11). Accordingly, one must be wary of the manner in which emission measurements are made.

In a recent review, workers at Battelle compared NO_x data from a number of laboratories and, in almost all cases, the emissions are less than the

EPA New Source Performance Standard which is 0.7 pound per million Btu heat input, maximum 2-hour average expressed as NO_2 (equivalent to approximately 550 ppm NO_2 at 3 per cent O_2 in the flue gas) (13).

At higher pressures (6 to 8 atm), experiments indicate NO_x levels are reduced to values on the order of 100 to 200 ppm, although the reason for lower values is not yet known (14,15).

SULFUR OXIDES EMISSIONS

Only brief attention will be paid here to SO_x emissions as their role in oxidant formation is considerably less well defined than that of HC or NO_x. The emissions of SO_x depend markedly on the calcium/sulfur (Ca/S) mole ratio which in turn is dependent on the amounts and types of coal and limestone used in the bed. In general, however, with Ca/S mole ratios greater than 2.0, 90 per cent control of SO_2 emission is achievable. By way of example, experimental results indicate that a bituminous coal with a heating value of 13,700 Btu per pound and a 2.8 per cent sulfur content when burned in a fluidized bed at velocities of 2.1 feet per second and a Ca/S ratio of 2.9 has an emission factor of 0.23 pound $SO_2/10^6$ Btu compared with EPA's New Source Performance Standard of 1.2 pounds $SO_2/10^6$ Btu (14).

CONCLUSIONS

Concentration estimates for the various types of pollutants that could form in coal-fired fluidized bed combustion are provided in Table 2 (16). As mentioned previously, there is only sparse experimental information available for most of these compounds and these estimates which are based on simple thermodynamic considerations and empirical correlations with conventional combustion systems are probably good only to within an order of magnitude. The only compounds generated in quantities high enough to be of concern in oxidant formation are NO, SO_2, and carbon monoxide (CO). The concentrations of these compounds, however, are significantly less than those generated in conventional combustion; hence, with respect to reducing oxidant formation, fluidized bed combustion is a promising alternative to present boiler systems.

Most of the existing data, however, has been gathered on bench scale equipment or small pilot plant systems. Final acceptance of FBC will probably await tests on larger facilities; but, presently, no emission problems are anticipated in the scaling up of the smaller facilities.

TABLE 2. ESTIMATED CONCENTRATION RANGES OF POTENTIAL POLLUTANTS FROM COAL-FIRED FLUIDIZED BED COMBUSTION (16)

Gas phase	
Several hundred parts/million:	CH_4, CO, HCl, SO_2, NO
Ten parts per million:	SO_3, C_2H_4, C_2H_6
One part per million:	HF, HCN, NH_3, $(CN)_2$, COS, H_2S, H_2SO_4, HNO_3, F, Na
One part per billion:	Diolefins, aromatic hydrocarbons, phenols, azoarenes, As, Pb, Hg, Br, Cr, Ni, Se, Cd, U, Be
One-tenth (0.1) part per billion:	Carboxylic acids, sulfonic acids, polychlorinated biphenyls, alkynes, cyclic hydrocarbons, amines, pyridines, pyroles, furans, ethers, esters, epoxides, alcohols, ozone, aldehydes, ketones, thiophenes, mercaptans
Solids	
One part per million:	Al, Ca, Fe, K, Mg, Si, Ti, Cu, Zn, Ni, U, V
One part per billion:	Ba, Co, Mn, Rb, Sc, Sr, Cd, Sb, Se, Ca
One-tenth (0.1) part per billion:	Eu, Hf, La, Sn, Ta, Th

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EMISSIONS ASSESSMENT OF THE CHEMICALLY ACTIVE FLUID BED (CAFB) PROCESS

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ABSTRACT

Stack gas and particulate emissions from the Chemically Active Fluid Bed pilot plant at the Esso Research Centre, Abingdon, were measured during gasification of fuel oil and bitumen. Quantities measured included total particulate, particulate size distributions, nitrogen oxides, sulfur oxides, and gaseous organic compounds. Both particulate and gaseous emissions were analyzed for organic functional groups using liquid chromatography and infrared spectroscopy. In addition, bulk and surface trace metal compositions of particulate were determined from spark source mass spectroscopy and X-ray photo-electron spectroscopy. Results are presented which indicate that satisfactory control of gaseous species is accomplished by this process but that additional particulate control is required.

INTRODUCTION

We report here on the results of an experimental emissions assessment of the Chemically Active Fluid Bed (CAFB) process which was developed by the Esso Research Centre, Abingdon (ERCA), England, as a means to generate electrical energy cleanly from high sulfur, high metal heavy fuel oil. In this technique, oil is vaporized in a fluidized bed of lime to produce a low Btu, low sulfur gas which is then burned in a conventional boiler. Most of the sulfur and some metals are captured by the lime.

At present, the only existing CABF unit is a 2.93 megawatt (MW) pilot plant at the ERCA facility (1). Foster-Wheeler Energy Corporation (F-W) is in the final design and procurement stages of a 10 MW retrofit demonstration plant to be constructed in San Benito, Texas, at the La Palma Station of the Central Power and Light Company (2). In addition, F-W has developed a conceptual design for a 250 MW commercial scale unit (2).

The emissions measurement program conducted at the ERCA facility was part of a multi-media environmental assessment sponsored by EPA and carried out by GCA to evaluate the overall environmental impact of this new process (3). The results of this program are to be used to provide guidance on measures which must be taken to minimize the environmental impact of the CAFB and suggest follow-up investigations which should be undertaken to in-

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sure the environmental acceptability of this process. To attain these goals, a systematic evaluation of all waste streams from the CAFB was made and a process emissions inventory was compiled. These data were derived from engineering estimates and from an extensive pilot plant field sampling and laboratory analysis program. Emission rates determined for the pilot plant were then used to predict pollutant loadings for the CAFB demonstration plant and proposed commercial units and to make recommendations for additional control requirements.

The experimental phase of the project consisted of two parts: a field test program carried out at the ERCA pilot plant during the period December 3 - 11, 1975, which consisted of on-site determinations of air emissions and collection of gaseous and solid samples; and a laboratory analysis program to identify and, where possible, quantify chemical constituents of samples collected at the pilot plant.

THE CAFB PROCESS

Figure 1 is a schematic diagram of the CAFB pilot plant and Table 1 lists mass flow rates and temperatures of internal and external streams. Limestone and oil are fed continuously into the gasifier at a calcium (Ca)/ sulfur (S) (limestone/oil) molar ratio of unity. In the gasifier, limestone ($CaCO_3$) is rapidly converted to lime (CaO) and carbon dioxide (CO_2), and the CaO is maintained in a fluidized state by a preheated air/flue gas mixture. The air input rate is roughly 20 percent stoichiometric with respect to oil. Fuel oil is consecutively vaporized, oxidized, cracked and reduced at 870°C (1600°F) to produce a low Btu gas. Over 80 percent of the input feed sulfur is removed by the lime. The gas travels from the gasifier through cyclones for particulate removal and then into a boiler for combustion. The boiler flue gas encountered a knockout baffle and another cyclone before entering the stack. Lime is continuously cycled between the gasifier and the regenerator where the roughly 7 percent of the lime which is sulfided in the gasifier is oxidized to CaO. At the pilot plant, sulfur dioxide (SO_2) produced in the regenerator is fed to the boiler stack. (In the demonstration plant, SO_2 will be fed to another unit which will reduce the sulfur (S) to its elemental form.) Some spent CaO is continuously withdrawn from the regenerator and retained for disposal. To maintain S removal efficiency, an equivalent amount of $CaCO_3$ is continuously added to the gasifier. Proper disposal of spent $CaCO_3$ is a major environmental concern.

FIELD TEST PROGRAM

Coincident with the planning and pre-test site visit was the announcement of the "multilevel phased approach" to source sampling and analysis by the Process Measurement Branch of the Industrial Environmental Research Laboratory, EPA (4). Because this project was a preliminary environmental assessment of a facility which heretofore had not been subjected to a comprehensive emissions assessment, the decision was made to combine measurements of the so-called criteria pollutants using the standard EPA methods with the new procedures for broad identification of organic and inorganic emissions.

The field test program was carried out at the ERCA pilot plant location

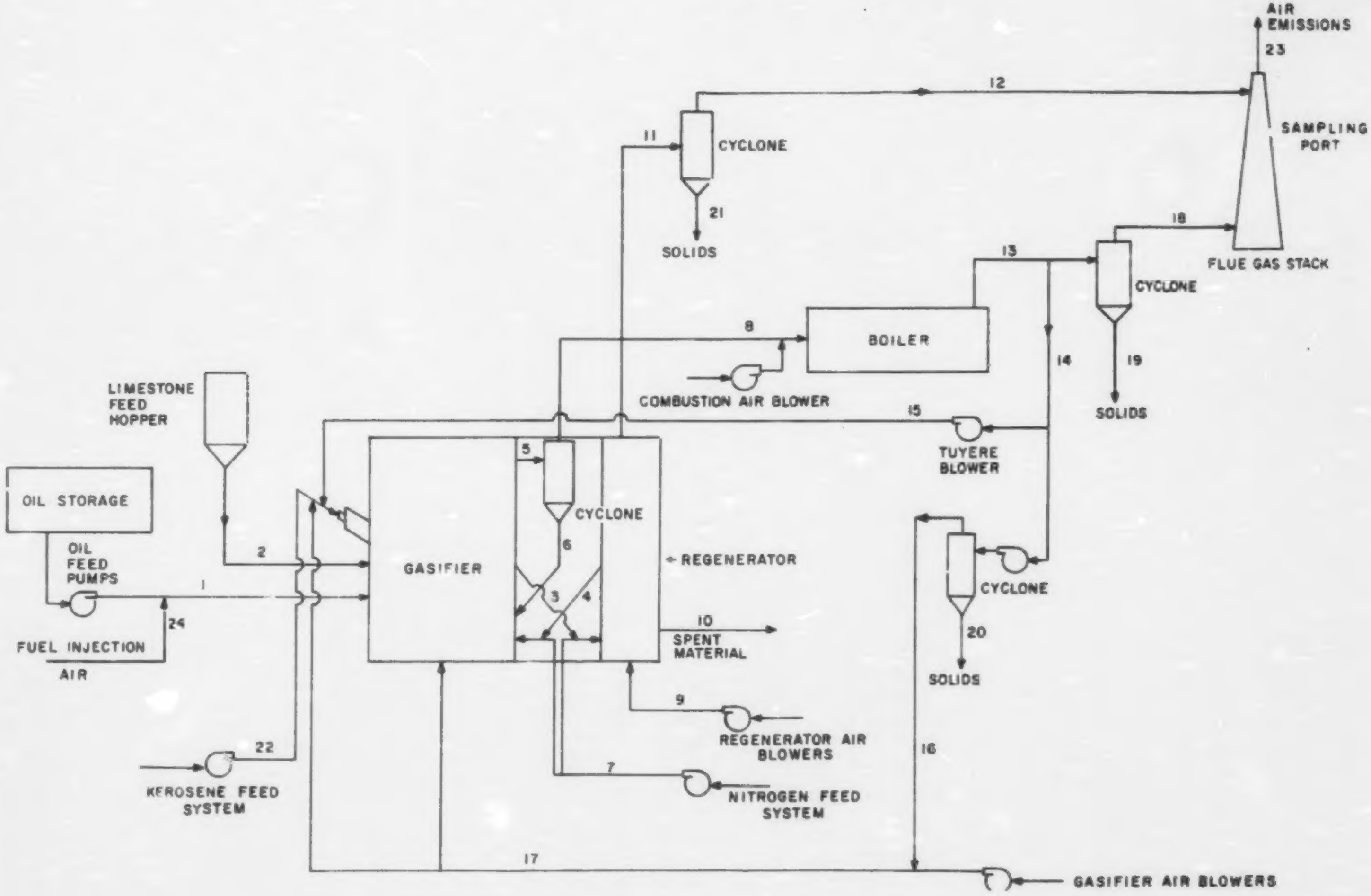

Figure 1. Unit operations flow diagram of the ERCA pilot plant. (Process streams are identified in Table 1.)

TABLE 1. ERCA PILOT PLANT MASS FLOW RATES

No. on Fig. 1	Process stream	Mass flow rate, kg/sec	(lb/hr)	Temperature, °C	(°F)
1.	Oil feed to gasifier	0.04	(228)	88	(190)
2.	Limestone feed to gasifier	0.003	(25)		
3.	Gasifier to regenerator stone transfer	0.11	(860)		
4.	Regenerator to gasifier stone transfer	0.11	(850)		
5.	Product gas to cyclone	0.16	(1,279)	850	(1,560)
6.	Cyclone solids return to gasifier				
7.	N_2 gas to solids transfer lines	0.0006	(4.5)		
8.	Product gas to boiler	0.16	(1,279)	850	(1,560)
9.	Air to regenerator	0.01	(65)		
10.	Spent solids from regenerator	0.002	(14)		
11.	Regenerator off gas to cyclone	0.01	(63)	1,050	(1,920)
12.	Regenerator off gas, cyclone to stack	0.01	(63)	1,050	(1,920)
13.	Flue gas from boiler	0.50	(4,000)		
14.	Flue gas recirculated to gasifier	0.03	(250)		
15.	Flue gas to Tuyere Blower	0.02	(125)		
16.	Recycled flue gas from cyclone	0.02	(125)		
17.	Flue gas and air to gasifier	0.10	(800)		
18.	Flue gas to stack	0.50	(4,000)		
19.	Solids from boiler flue gas cyclone				
20.	Solids from recycled flue gas cyclone				
21.	Solids from regenerator off gas cyclone				
22.	Start up kerosene to gasifier	0.0005	(4)		
23.	Stack emissions	0.50	(4,000)	43	(110)
24.	Fuel injection air	0.01	(45)		

during December, 1975. During this period, two fuel oils were fired: bitumen (vacuum bottoms) and residual oil (atmospheric bottoms). Samples were collected during seven separate runs: four residual oil gasification runs; two bitumen gasification runs; and one combustion/startup bitumen run. The field measurement program consisted of on-site quantification of SO_2, sulfur trioxide (SO_3), nitrogen oxides (NO_x), hydrogen sulfide (H_2S), total particulate and particulate size distributions. Flue gas was sampled and analyzed for NO_x by Method 7, SO_2/SO_3 by Method 8 and H_2S by Method 11 (5). An Orsat analyzer was used to measure carbon monoxide (CO), CO_2 and oxygen (O_2). Particulate sampling was accomplished using a standard RAC train constructed according to the procedures outlined in EPA Method 5 (5). Due to the positions of the installed ports, eight point traverses were taken on two diameters 120 degrees apart. The train was modified slightly to allow for sampling of gaseous organic species (see below). Particulate size distribution measurements were taken with a University of Washington eight stage instack impactor using ungreased foil substrates. A single point was sampled isokinetically for sufficient time (15 to 30 minutes) to collect a weighable quantity on each stage.

In addition to collection of particulate and inorganic gases, organic vapors were collected in a specially designed adsorbent trap placed between the filter and the impingers on the Method 5 train. The polymer used in this adsorbent cell, Tenax, reportedly retains all organic gases larger than C_5.

LABORATORY ANALYSIS PROCEDURES

Three general types of analytical procedures were applied to oil, flue gas, and particulate samples collected during the field test program: organic functional group identification; trace element quantification; and surface element and inorganic compound quantification.

ORGANIC FUNCTIONAL GROUP ANALYSIS*

In this procedure, sample extracts are separated into eight fractions by liquid chromatography (LC), evaporated to dryness, weighted, redissolved, and analyzed by infrared spectroscopy (IR) (6). Methylene chloride was used to extract oil and particulate samples whereas pentane was used to extract organic vapors adsorbed on the Tenax polymer.

Liquid chromatographic separation into eight fractions is accomplished by transferring the extract to an LC column and eluting sequentially with a series of solvent mixtures. After collection from the LC column each fraction is reduced to dryness using a Kuderna-Danish evaporator and air evaporation and then weighed to determine the amount of organic material in each fraction.

The dried fractions are then redissolved in methylene chloride and subjected to IR analysis. The IR spectra are then scanned for functional group peaks.

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*These analyses were performed by Battelle Columbus Laboratories under subcontract and by the Process Measurements Branch of EPA.

TRACE ELEMENT ANALYSIS*

Stack particulate was analyzed for bulk elemental composition using low precision (±200 percent) spark source mass spectrometry (SSMS). This technique is sensitive to 70 elements. To calibrate the SSMS results, some elements were quantified by higher precision atomic absorption (AA) spectroscopy. Interference of organic ions with low atomic weight elements is well known in SSMS as are losses of volatile compounds. Thus uncertainties of values derived for light elements such as fluorine, sodium and sulfur may be higher than the indicated precision.

SURFACE ANALYSIS

A number of particulate samples were investigated for surface elements and inorganic compounds by X-ray photoelectron spectroscopy (XPS or ESCA). All samples analyzed by ESCA in this study were first scanned over the entire electron binding energy range (broadband scan) to identify those elements present in concentrations greater than 0.1 percent. These broadband spectra were then analyzed to yield surface concentrations of all identifiable elements. The compound forms of surface vanadium and sulfur are also of interest in this study. They were investigated by scanning the binding energy ranges corresponding to the ejection of the 2p electron of vanadium and the 2p electron of sulfur. To supplement the bulk SSMS analyses, high energy argon ions were used to etch away surface layers exposing strata 20 to 100 Å deep. The exposed sample layers were then rescanned over the entire binding energy range and the resultant elemental concentrations were compared with the surface values and the SSMS analyses.

FIELD TEST RESULTS

Table 2 summarizes the stack emission rates of NO_x, SO_2, SO_3, H_2S, and total particulate. The average NO_x concentration of 53.5 ppm is considerably lower than the low end of the concentration range found for conventional oil- and gas-fired boilers. The measured emission rate is also about one-fourth of the New Source Performance Standard (NSPS) for oil-fired boilers and one-third of the NSPS for gas-fired boilers (7). Furthermore, the relative invariance of the three measurements suggests a low correlation between the NO_x emission rate and temperature, excess oxygen, bed stone history, and fuel.

Several factors may contribute to the low absolute NO_x emission rate. The reducing atmosphere in the gasifier may severely inhibit oxidation of fuel nitrogen. It has also been suggested that $CaCO_3$ might aid catalytically in the decomposition of NO or react directly with NO (8). The presence of nitrogen on the surface of some of the smaller particulate (which was noted in the ESCA analysis) is consistent with this latter mechanism. It is also possible that reduced nitrogen species, such as ammonia (NH_3), formed in the gasifier, pass through the boiler without reacting. It is more difficult to explain away the apparently small amount of NO formed by thermal fixation in

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*This work was performed by Battelle Columbus Laboratories and Aculabs under subcontract to GCA and by Northrop Services under contract to EPA.

TABLE 2. SUMMARY OF STACK EMISSIONS

		NO_x		SO_2		SO_3		H_2S		Total particulate	
Run	Fuel	ppm	$lb/10^6$ Btu	ppm	$lb/10^6$ Btu	ppm	$lb/10^6$ Btu	ppm	$lb/10^6$ Btu	ppm	$lb/10^6$ Btu
1	Fuel Oil	53.5	0.0851	292	0.6431	8.3	0.023	<0.05			0.0971
2	Fuel Oil	45.7	0.0671	305	0.6191	7.9	0.0201	<0.05			0.0561
3	Fuel Oil							0.23	$2.6x10^{-4}$		0.063
4	Fuel Oil										0.0921
5	Bitumen	58.4	0.0791	828	1.5624	11.1	0.0263				0.101
6	Bitumen and Stone Feeding										0.1046
7	Bitumen										0.1921

the boiler. The use of the thermal fixation reaction is strongly affected by boiler design and firing characteristics which cannot easily be evaluated.

Two uncertainties are thus apparent. What is the fate of the fuel bound nitrogen which is not converted to NO_x? How will the rate of the thermal fixation reaction be affected by the particular characteristics of the boiler to be used in conjunction with the demonstration plant?

The SO_2 emission rates for residual oil gasification were about 20 percent below NSPS for oil-fired steam generators and correspond to retention of 80 percent of the fuel sulfur in the gasifier lime (7). The higher SO_2 rate measured for bitumen gasification is due to two factors: the sulfur content of bitumen is roughly 50 percent higher than in fuel oil and, more importantly, stone present in the gasifier during this run had been unregenerated and unreplenished for some time because of clogging in the gasifier-regenerator transfer duct.

The primary source of particulate emissions from the CAFB is gasifier bed stone which passes through the two internal cyclones, the knockout baffle, and the stack cyclone. The NSPS for particulate emissions from oil-fired boilers is 0.1 $lb/10^6$ Btu (7). Table 2 shows that during oil gasification two of the four runs produced emissions only a few percent below the standard. The NSPS was exceeded during bitumen gasification and combustion; the final bitumen gasification run exceeded the particulate standard by a factor of two.

Two factors must be invoked to understand the variation in and magnitude of particulate emissions: cyclone efficiency and fresh stone feed. The cyclones used at the pilot plant were not designed specifically for the CAFB and operated at an efficiency of only 50 percent. The high emission rate from Run 7 can be attributed to an unusually high fresh stone feed rate. Fresh stone undergoes attrition and calcination as it enters the gasifier. High stone feed rate normally occurs during start up (combustion) but was employed during Run 7 to compensate for the buildup of saturated stone due to the clogging of the gasifier-regenerator stone transfer duct. The particulate sizing distributions measured during Runs 3 and 5 indicate that a substantial fraction of the particulate emissions is in the respirable range and hence of primary concern. The large respirable fraction is typical of conventional cyclones and may be expected in emissions from the demonstration plant which will also employ cyclones for particulate control.

LABORATORY ANALYSIS RESULTS

The laboratory program consisted of organic and inorganic analyses of stack particulate and organic analyses of flue gas, bitumen, and spent regeneration stone. Stack gas emissions collected during bitumen gasification were found to contain aliphatic hydrocarbons, alcohols, ketones, aromatics and carboxylic acid salts. The total gaseous organic emission rate ($C>5$) was 0.022 lb/10^6 Btu. Particulate from this same run contained aliphatic hydrocarbons, carbonyl compounds, esters, aromatics, phthalates, phenols and alcohols totaling 7×10^{-5} lb/10^6 Btu.

Elemental analyses of these stack particulates indicated that the most abundant species are: calcium, 14.1%; sulfur, 3.9%; vanadium, 1%; silicon, 0.5%; sodium, 0.4%; magnesium, 0.3%; nickel, 0.2%; and iron, 0.1%. Comparison of these values with EPA's Multi-Media Environmental Goals (MEG's)(9), which are derived from TLV's, showed that only the vanadium emission rate is of potential concern. Compound identification by ESCA showed that particulate vanadium exists as a mixture of oxides, V_2O_5, VO_2 and V_2O_3.

Particulate from fuel oil gasification was found to contain aliphatic hydrocarbons, carbonyls, esters, ketones, aldehydes, alcohols and carboxylates. The total organic particulate emission rate was approximately equal to that from bitumen gasification. The elemental composition of these particulates is similar to the bitumen particulates but contains half as much sulfur and roughly 0.15% of chlorine and fluorine.

CONCLUSIONS

The CAFB process was developed to control sulfur oxide emissions from combustion of high sulfur heavy fuel oil. The results presented here show that this goal can be met under proper system operating conditions. Under the upset mode in which gasifier stone becomes saturated, control effectiveness of the process is impeded.

Particulate emissions present the most pressing air pollution problem. Even under normal operation the particulate emission rate, caused by attrition of gasifier bed stone, approaches the NSPS for oil-fired units. Improved particulate collection efficiency is required and is being developed, in the form of more highly efficient cyclones, for the demonstration plant presently in the final design state (2).

Nitrogen oxide emissions from the CAFB are very low and appear to be independent of fuel, gasifier stone history, and detailed operating conditions. The reasons for this observation are not understood completely and additional studies should be undertaken to uncover the fate of fuel nitrogen.

Gaseous and particulate organic stack emission rates do not appear to present any significant problem. Vanadium is the only trace element whose emission rate is potentially harmful. However, control of total particulate emissions will significantly reduce vanadium output.

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NO_x CONTROL BY ABSORPTION

G. Sakash*

ABSTRACT

The elimination of nitrogen oxides fumes exhausted from a uranium scrap recovery operation is accomplished by the chemical conversion of nitrogen oxides to nitrogen dioxide using pure oxygen, and a subsequent absorption of the nitrogen dioxide by rapidly recirculating water to form nitric acid. An excess of pure oxygen fed from a cryogenic system is used to completely convert all of the nitrogen oxide gas to nitrogen dioxide. The excess oxygen is the only gas ultimately discharged to the atmosphere. The nitric acid formed by the absorption process is recirculated until the desired concentration is obtained. The acid is then pumped back to the scrap recovery system for reuse.

INTRODUCTION

The high toxic hazard rating associated with oxides of nitrogen (NO_x) are of major concern to all manufacturing facilities where the potential of NO_x fume emission exists.

It is the intent of this paper to describe a process which has successfully eliminated the NO_x fumes emitted from the dissolution of uranium dioxide in nitric acid.

The process chemically converts NO_x to nitrogen dioxide (NO_2) using pure oxygen; the NO_2 is concurrently absorbed by rapidly recirculated scrubbing water to form nitric acid. The process utilizes an excess of pure oxygen to completely convert all of the NO_x gases to NO_2 which is very soluble in water.

This process has been in use at the General Electric Company in Wilmington, North Carolina, for three years. It has completely eliminated all visual NO_2 fumes and reduced the NO_2 emission level to less than 5 ppm which is the current Threshold Limit Value (TLV) as published by ACGIH.

DISCUSSION

In the reclamation of scrap uranium dioxide, the scrap material is dissolved in nitric acid. During this dissolution process, large quantities of gaseous vapors, in the form of nitric oxide (NO) and NO_2, are evolved. These gases are identified as NO_x and are exhausted as a brownish plume, creating a very undesirable atmospheric pollution condition.

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The TLV for NO, as published by ACGIH, is listed at 25 ppm or 30 mg/m^3 of air. The NO_x fumes exhausted during the uranium dioxide dissolution process is far in excess of this; therefore, it was necessary to devise a process which would reduce this emission to an acceptable level. This was accomplished by the utilization of a device (Figure 1) in which oxygen and water convert the NO_x fumes into nitric acid. This device consists of a conversion chamber where the NO_x are converted to NO_2 and an absorption chamber where the NO_2 is converted to nitric acid. An excess of pure oxygen, fed from a cryogenic system, is used to completely convert all of the NO_x gases to NO_2. The excess oxygen is the only gas ultimately discharged to the atmosphere.

The absorption column, constructed of 317 stainless steel, measures 20 feet high and 4 feet in diameter and is divided into three compartments. The top five-foot section is used as the conversion chamber where the chemical conversion of the NO_x to NO_2 takes place. The oxidation reaction occurs readily at room temperature without a catalyst. The middle ten-feet of the column is used as a mixing chamber. This portion of the column is filled with ceramic Intelox packing. In this portion of the column, the water and NO_2 mix to form nitric acid. The bottom five-feet of the column is the acid accumulation chamber.

The scrubbing water, flowing at a rate of 250 gpm, is continually recirculated through the absorption column until the acid concentration is increased to a reusable product. The heat of reaction is controlled by passing the recirculation solution through a stainless steel heat exchanger. Continuous monitoring of the acid concentration is done at a main control panel. After the required acid concentration is reached, the acid is pumped back into the dissolvers for reuse.

The off gas consisting mainly of excess oxygen is drawn up through a high efficiency filter housing, then through a Buffalo gas absorber scrubber, and finally through another bank of high efficiency filters. A Leeds and Northrup NO_x emission monitor is installed in the off gas stack and continuously monitors and records the visible NO_x fumes being exhausted out the stack. An alarm automatically sounds if a malfunction in the absorption system occurs.

Because the system is used in the reclamation process of radioactive uranium dioxide scrap, constant monitoring for radioactive material is required. This is done both on the recirculation solution by periodic laboratory analysis and on the exhaust gases by continuous stack exhaust monitoring.

Chemically, the major reactions which take place during the absorption are as follows:

$$\begin{array}{l} 3NO + 1\tfrac{1}{2}\, O_2 \longrightarrow 3NO_2 \\ 3NO_2 + H_2O \longrightarrow 2HNO_3 + NO \\ \hline 2NO + 1\tfrac{1}{2}\, O_2 + H_2O \qquad 2HNO_3 \end{array}$$

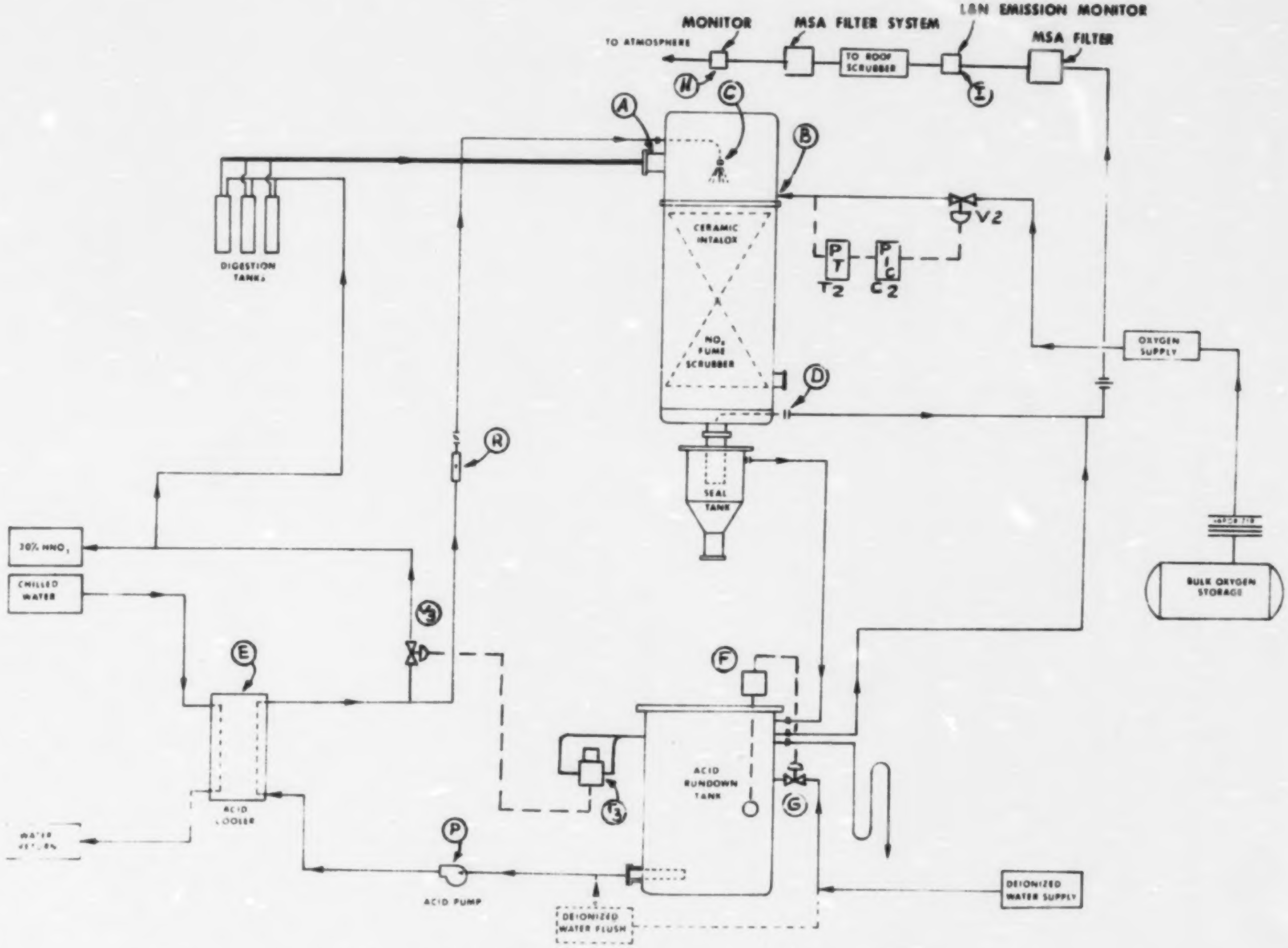

Figure 1. NO_x absorption process utilized by the General Electric Company.

The process (Figure 1) occurs as follows:

1. Uranium dioxide is dissolved in nitric acid in the dissolution chambers.

2. NO_x gas generated by dissolution leaves the top of the dissolution chambers and enters the absorption column at A.

3. Pure oxygen from the cryogenic oxygen system enters the absorption chamber at B. When additional oxygen is required, it is automatically added through the pressure sensing V_2, C_2, T_2 system.

4. A water-acid mixture recirculating through pump, P, and heat exchanger, E, enters the absorption chamber through a spray nozzle at C. Rotometer, R, indicates flow.

5. The excess oxygen is exhausted as spent gas through D and goes through absolute filters prior to exhausting to the atmosphere.

6. As the concentration of the nitric acid formed is increased, it is sensed through T_3; and when the desired concentration is reached, it is automatically pumped through control valve V_3 into the dissolvers.

7. Make-up deionized water enters the acid storage tank at G. A level is automatically maintained by a float controller at F.

8. A Leeds and Northrup NO_x emission monitor, I, senses visual emission and records it at a remote control panel.

9. A monitor, H, continuously monitors the off gas for radioactive particulate.

It is conceivable that this system could be adapted to any facility where control of NO_x emission is a problem.

DEVELOPMENT OF A LOW EMISSIONS PROCESS FOR ETHYLENE DICHLORIDE PRODUCTION

W.S. Amato, B. Bandyopadhyay, B.E. Kurtz, and R.H. Fitch*

ABSTRACT

This work covers the initial phase of the development of a low-emissions ethylene oxyhydrochlorination process for producing 1,2 dichloroethane (ethylene dichloride).

Firstly, experimental work on an existing pilot plant scale, once-through process was used to obtain baseline emission data in mass of hydrocarbon plus ethylene dichloride per mass of hydrogen chloride fed as a function of reactor temperature and percent excess ethylene to the reactor; and to resolve potential problems which may arise in a recycle operation, viz., whether carbon monoxide is oxidized to carbon dioxide by the reactor, whether post-chlorination might be necessary in order to save ethylene value in the reactor exit if a carbon monoxide oxidation unit were necessary, and whether the reactor would oxidize methane and ethane, thereby preventing their buildup in the recycle system.

Secondly, the existing once-through pilot plant was converted to a recycle operation which then functioned successfully and yielded emission data in mass of hydrocarbon plus ethylene dichloride per mass of hydrogen chloride fed as a function of reactor temperature and percent excess ethylene to the reactor. In particular, the project objective of reducing by 90 percent the hydrocarbon plus ethylene dichloride emissions from an ethylene oxyhydrochlorination process, through the recycling of reactor off-gases, has been positively demonstrated.

Thirdly, various operating difficulties were assessed which would be important for future control applications and scale-up efforts, viz., the increased sensitivity of the process to upsets in flows, temperatures, and concentrations.

Lastly, economic analyses are presented to demonstrate the competitive position of the improved process.

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INTRODUCTION

The production of vinyl chloride in the United States is almost exclusively based on ethylene (C_2H_4) and involves three main steps:

direct chlorination of ethylene:

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2 \ ,$$

oxyhydrochlorination of ethylene:

$$C_2H_4 + 2\ HCl + 1/2\ O_2 \longrightarrow C_2H_4Cl_2 + H_2O, \text{ and}$$

cracking of ethylene dichloride:

$$2\ C_2H_4Cl_2 \longrightarrow 2\ C_2H_3Cl + 2\ HCl$$

The overall reaction in this balanced process is:

$$2\ C_2H_4 + Cl_2 + 1/2\ O_2 \longrightarrow 2\ C_2H_3Cl + H_2O.$$

The oxyhydrochlorination step is the most technically difficult part of the overall process and has had a profound impact on the industry since its development. The first commercial ethylene oxyhydrochlorination process appeared in 1964 and within the next few years nearly 90 percent of the classical process for vinyl chloride from acetylene was displaced.

EXISTING PROCESS

There are currently two basic variants of ethylene oxyhydrochlorination processes, those employing fixed catalytic beds and those employing fluid catalytic beds. Most of the major producers employ a fluid bed. Ethylene (C_2H_4), hydrogen chloride (HCl), and air are introduced into the bottom of the fluid bed where the oxyhydrochlorination reaction takes place. The heat released by the reaction is substantial, so the reactors are equipped with internal cooling coils which are submerged in the fluid bed.

Downstream product recovery involves cooling of the reactor exit gases by either direct quench or a heat exchanger, followed by condensation of the ethylene dichloride (EDC) product and water by-product which are separated by decantation. The remaining gases still contain 1 to 5 percent by volume of EDC, so they are further processed in a secondary recovery system employing either solvent absorption or a refrigerated condenser. The offgas is then vented to the atmosphere. (See Figure 1.)

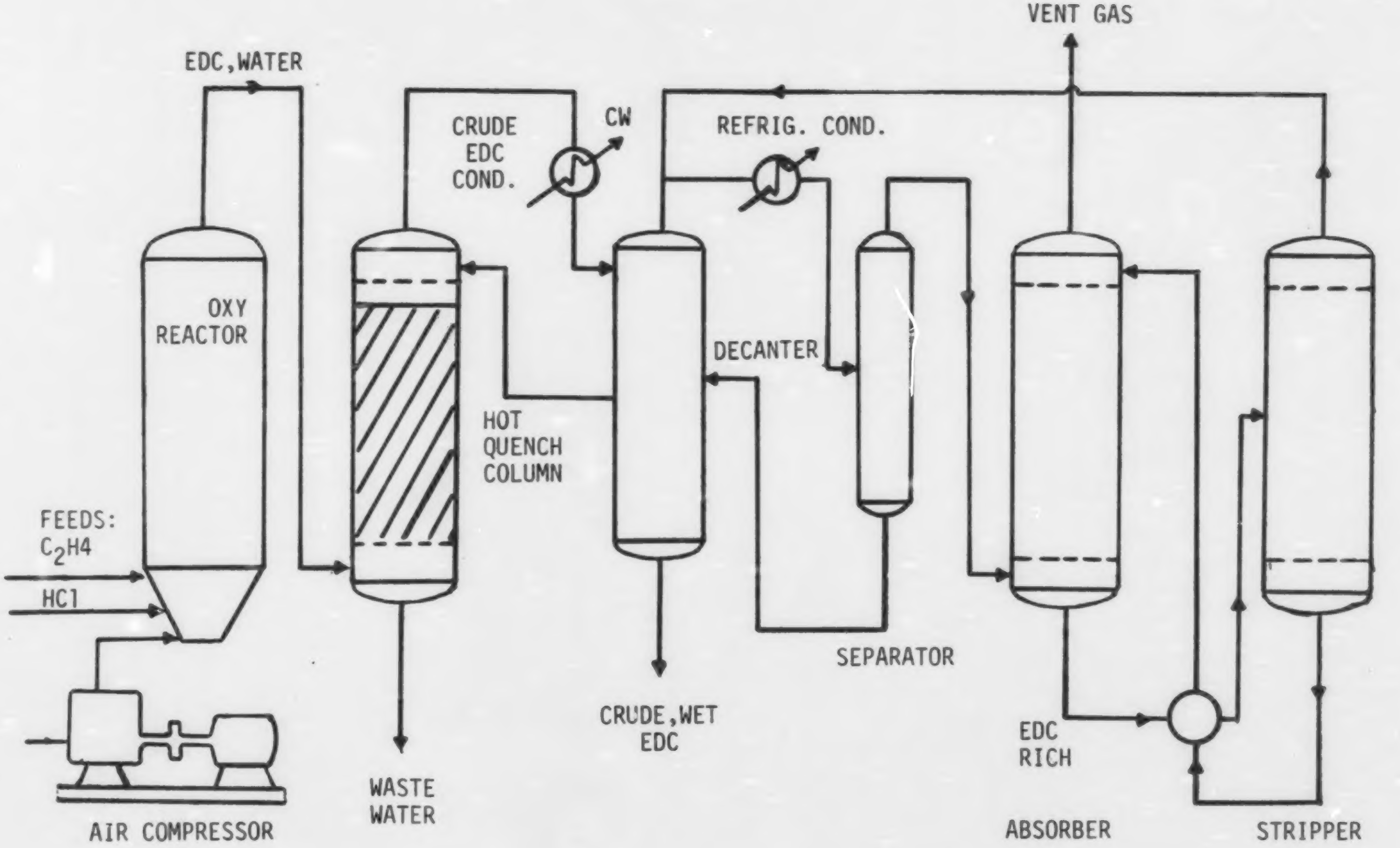


Figure 1. Flowsheet for existing ethylene oxyhydrochlorination process.

The vent stream contains 85 to 95 percent nitrogen from the air employed as a source of oxygen for the oxyhydrochlorination reaction. It also includes a variety of other compounds which originate either in the feeds to the reactor or as by-products of the oxyhydrochlorination, such as carbon dioxide, carbon monoxide, EDC, C_2H_4, methane (CH_4), ethane (C_2H_6), ethyl chloride and absorber solvent.

The aspect of most current ethylene oxyhydrochlorination processes which contributes the most to hydrocarbon (HC) emissions is the use of air as the source of oxygen. The inerts (nitrogen) accompanying the air necessitate a once-through process. If pure oxygen were used it would be possible, at least in theory, to recycle the reactor off-gases. Only one plant currently employs pure oxygen, but it does not recycle the reactor off-gases.

PROPOSED PROCESS

Recycle of reactor off-gases will eliminate the need for a secondary recovery system and the resultant losses of solvent which typically amount to 0.001 ton per ton of EDC. It will also eliminate unreacted C_2H_4. Some means will have to be employed to limit build-up of feed impurities (CH_4 and C_2H_6) and by-products (CO_2, CO, and ethyl chloride), probably a combination of removal by chemical or physical processing and a purge to atmosphere. The purge, however, will amount to only a small fraction of the vent stream which characterizes present processes and it is certainly reasonable to expect a 90 percent reduction in HC emissions over present processes.

The detailed technical approach currently visualized may best be explained by reference to Figure 2.

A fluid bed oxyhydrochlorination reactor employing a conventional copper chloride on alumina catalyst is fed with C_2H_4, HCl, and recycle gas containing added oxygen. The C_2H_4 is in 5 percent excess over that required by the reaction stoichiometry, the oxygen in 60 to 80 percent excess. Near the top of the fluid bed a small stream of chlorine, amounting to 2 to 5 percent of the HCl feed, is added to convert the unreacted C_2H_4 to additional EDC.

The gases leaving this reactor contain the products of reaction, EDC and water, and other substances originating as unreactive impurities in the feeds or as by-products. The gases pass to a quench column where they are cooled by circulating water, then to a condenser where EDC and water are recovered. These are separated in a decanter and the non-condensable gases flow through a recuperative heat exchanger where they are re-heated.

The hot gases pass to a fixed bed oxidation reactor (shown dashed) employing a platinum on alumina catalyst where the CO will be converted to CO_2 by reaction with the excess oxygen from the oxyhydrochlorination reactor. The gases exiting the reactor are cooled against the entering gases in the recuperative heat exchanger and passed to a booster compressor. It may be possible to eliminate the separate CO oxidation step if it can be shown that CO can be oxidized to CO_2 by recycle to the oxyhydrochlorinator. If this is possible, then the need for post-chlorination is obviated.

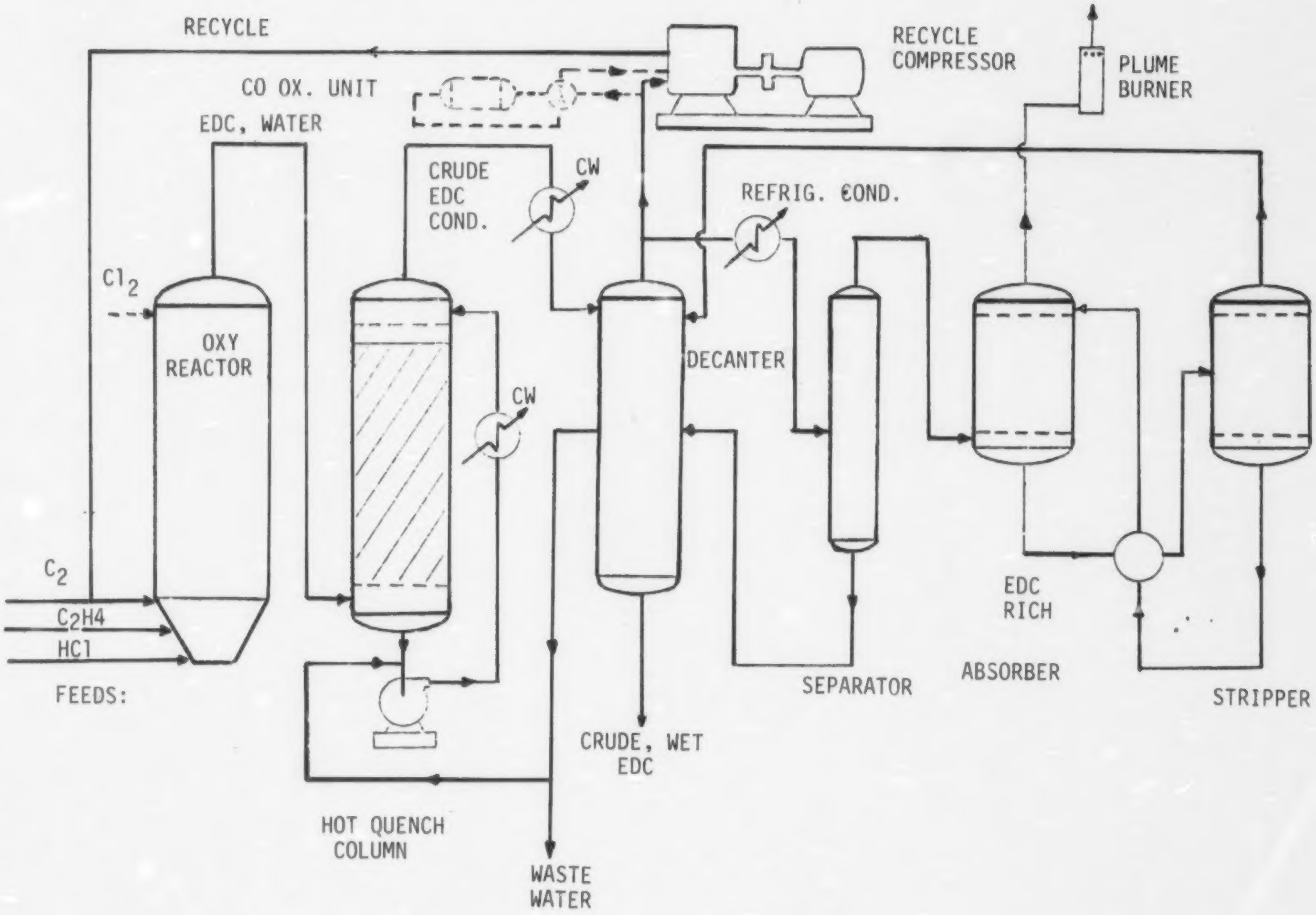


Figure 2. Flowsheet for proposed ethylene oxyhydrochlorination process.

The majority of the discharge from the booster compressor is recycled to the oxyhydrochlorinator. This recycle gas will be predominately CO_2 with the process as described here. A small portion of the recycle gas is purged in order to limit the build-up of unreactive impurities which enter the system with the reactor feeds, for example: CH_4 and C_2H_6 which are typical impurities in the C_2H_4.

This purge stream is first cooled in a recuperative heat exchanger and then further cooled in a refrigerated vent condenser which removes most of the EDC and ethyl chloride. These are collected in a receiver from which the purge gases, consisting of 80-90 percent CO_2 and 10 percent CH_4 and C_2H_6, are discharged through the recuperative heat exchanger and may be disposed of via incineration.

The net effect of this process will be at least a 90 percent reduction in HC emissions compared to typical present processes.

OBJECTIVE AND SCOPE OF PROJECT

The objective of the project was to demonstrate that emissions from the production of EDC by oxyhydrochlorination of C_2H_4 could be reduced in a modified process by at least 90 percent from the levels encountered with typical existing processes. The modified process was to employ recycle of reactor exit gas, oxygen feed, and whatever additional processing steps were determined to be necessary to control build-up of by-products in the recycle stream and was to be economically competitive with present-day processes. The process performance was to be evaluated on a laboratory scale and a preliminary study of technical and economic feasibility was to be carried out.

PRELIMINARY EVALUATION OF ALTERNATIVE APPROACHES

The preliminary evaluation of alternative approaches considered the following process alternatives: oxygen feed with vent gas recycle on the existing process; catalytic oxidation of vent gas; and thermal incineration of the vent gas. The results can be summarized as shown in Table 1.

The results of the economic evaluations of these alternatives show clearly that the oxygen addition with vent gas recycle on the existing process is by far the most economic choice. The estimates are based on a 700 MM lb/year EDC plant.

EXPERIMENTAL PROGRAM

The main chemical reactions which occur in fluid-bed oxyhydrochlorination of C_2H_4 are:

TABLE 1. PROCESS ALTERNATIVES

Economic Consideration	Process Oxy Feed - Recycle	 Thermal Incineration	 Catalytic Oxidation
Net Capital Increase	($1,300,000)*	$1,750,000	$2,250,000
Net Increase in Manufacturing Cost	$377,000/y	$695,000/y	$985,000/y
Unit Cost Increase, ¢/lb EDC	0.054	0.099	0.141

* Figures in parentheses refer to savings in capital.

Principal Reaction:

$$C_2H_4 + 2\ HCl + 1/2\ O_2 \xrightarrow[\text{Cupric Chloride Catalyst}]{} C_2H_4Cl_2 + 2\ H_2O \qquad (1)$$

Main Side Reactions:

$$C_2H_4 + 2\ O_2 \rightleftharpoons 2\ CO + 2\ H_2O \qquad (2)$$

$$C_2H_4 + 3\ O_2 \rightleftharpoons 2\ CO_2 + 2\ H_2O \qquad (3)$$

$$C_2H_4 + HCl \rightleftharpoons C_2H_5Cl \qquad (4)$$

$$2\ CO + O_2 \rightleftharpoons 2\ CO_2 \qquad (5)$$

QUESTIONS NEEDING RESOLUTION BEFORE FINAL DEVELOPMENT OF A RECYCLE PROCESS

Question 1: Will CO build-up in the recycle system reach levels which will cause explosive conditions?

Will the ratio of CO_2/CO remain at about 2 in the recycle system as it does in the once-through system?

Can the reactor system effectively oxidize CO to CO_2?

Question 2: If CO is not oxidized in the reactor, but is oxidized in a separate unit, how do we avoid the loss of C_2H_4 value by oxidation?

Question 3: Can post-chlorination effectively work on the exiting reactor gases to convert unreacted C_2H_4 to EDC?

Question 4: What is the effect of the reactor system on HC impurities, such As CH_4 and C_2H_6, which might occur in the C_2H_4 feed?

With these questions before us, the scope of an experimental program was evolved as follows:

SCOPE OF THE EXPERIMENTAL PROGRAM

1. Once-Through Runs

   (a) Baseline runs at 230-240°C with 5, 10, 15 percent excess C_2H_4 and 60-70 percent excess O_2 (as air).
   (b) Runs with CO and CO_2 additions.
   (c) Hydrocarbon additions: CH_4 and C_2H_6.
   (d) Post-chlorination work.

2. Recycle Runs (O_2 Feed)

   (a) Runs at 230, 240, 250°C with 5-20 percent excess C_2H_4 and 50-115 percent excess O_2 with vent rates of less than 10 percent of total off-gases.

RESULTS

The results of correlation of emissions data from the once-through process are:

$$\text{(Mean - 231°C)}\ EM_O = 2.47(10^{-2}) + 1.35(10^{-3})\ XSETH \tag{6}$$

$$\text{(Mean - 240°C)}\ EM_O = 1.32(10^{-2}) + 1.35(10^{-3})\ XSETH \tag{7}$$

Where

EM_O = Emissions in $\frac{kg(HC + EDC)}{Kg\ HCl}$ for once-through operation.

XSETH = Percent excess ethylene to reactor.

The results of correlation of emission data from the recycle process are:

$$\text{(Mean - 230°C)}\ EM_R = -1.08(10^{-4}) + 2.05(10^{-4})\ XSETH \tag{8}$$

$$\text{(Mean - 242°C)}\ EM_R = -6.45(10^{-4}) + 2.05(10^{-4})\ XSETH \tag{9}$$

$$\text{(Mean - 251°C)}\ EM_R = -8.03(10^{-4}) + 2.05(10^{-4})\ XSETH \tag{10}$$

Where

EM_R = Emissions in $\frac{\text{kg(HC + EDC)}}{\text{Kg HCl}}$ for recycle operation.

XSETH = Percent excess ethylene to reactor.

Comparison of the emissions from the once-through and recycle operation at the same reactor temperature and percent excess ethylene is shown in Table 2. Table entries show % reductions in emissions $-\eta$ of recycle process compared with once-through process at similar values of % excess ethylene and reactor temperature, T°C.

TABLE 2. COMPARISON OF EMISSIONS DATA, RECYCLE AND ONCE-THROUGH

Table entries show % reductions in emissions $-\eta$ of recycle process compared with once-through process at similar values of % excess ethylene and reactor temperature, T°C.

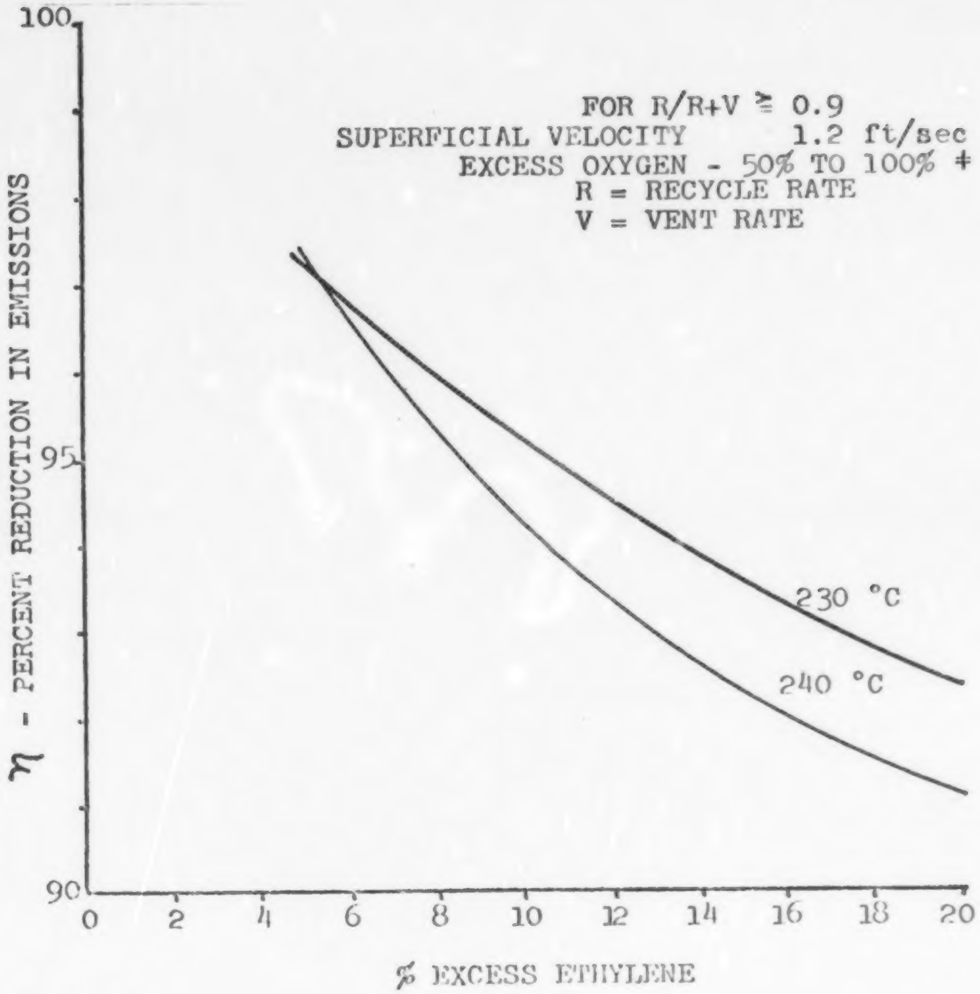
% Excess Ethylene	230°C	240°C
5	97.2	97.4
10	95.1	94.2
15	93.6	92.3
20	92.4	91.1

This result is also shown in Figure 3. Thus, it can be seen that the original objective of this investigation, viz., the reduction by 90 percent of the emissions from the EDC process through implementation of a recycle scheme has been positively demonstrated.

CONCLUSIONS

EXPERIMENTAL RESULTS OF ONCE-THROUGH OPERATION

- Crude ethylene dichloride (EDC) purity varied inversely linearly with reactor temperature.



‡ Most commercial plants operate at 50-70% excess air and 5-10% excess C_2H_4.

Figure 3. η - Percent reduction in emissions recycle compared to once-through vs. % excess ethylene with reactor temperature as parameter.

- Kilograms of HC plus EDC per kg of HCl emissions could be correlated as a linear function of excess C_2H_4 to the reactor with reactor temperature as parameter.
- Ethylene efficiency decreases with higher operating temperature due to increased oxidation of ethylene.

- Addition of CO to the feed gases indicated that CO was oxidized to CO_2; also large additions of CO_2 to the feed gases did not adversely affect the reaction.
- Methane passed through the reactor system unchanged and C_2H_6 was significantly reduced (80 percent in this case) over inlet values.
- Post-chlorination of excess C_2H_4 in the reactor exit gases was feasible provided chlorine was injected into the gas phase and not the catalyst itself.

EXPERIMENTAL RESULTS OF RECYCLE OPERATION

- Crude EDC purity varied inversely linearly with reactor temperature, but was a few tenths of a percentage point lower than the once-through purity at the same temperature.
- The C_2H_4 efficiency for the recycle operation was higher than that for the once-through process due to the recycling of off-gases.
- Ethylene efficiency decreases with higher operating temperature due to increased oxidation of ethylene.
- All runs of this report involved the recycling of greater than 90 percent of the reactor off-gases.
- Kilograms of HC plus EDC per kg of HCl emissions could be correlated as a linear function of excess C_2H_4 to the reactor with reactor temperature as parameter.
- The recycle operation is more sensitive than the once-through operation and requires closer control for successful operation.

COMPARISON

Comparison of the emissions data for once-through and recycle operation indicates that the percent reductions of HC plus EDC emissions have exceeded 90 percent for all runs conducted in this work.

It was possible to develop a computer simulation program, based on actual experimental data, which could duplicate vent gas compositions and superficial velocities at given reactor temperatures and pressures for given excess C_2H_4/oxygen values to the reactor. Based upon the optimum experimental conditions from recycle operation, viz., 230°C, 5-7 percent excess C_2H_4 and 50 percent excess oxygen, together with this simulation program, it was found that the recycle process was competitive with existing processes to within a tenth of a percent of total incremental capital and manufacturing costs.

The work of this report has revealed that the newly-developed recycle process is much more sensitive to upsets than the conventional once-through process.

Before a commercial prototype of the proposed process can be designed, these sensitivity factors must be more fully explored along with the establishment of well-defined requirements necessary for stable operation. Thus, it is recommended that further work be performed on the newly-developed recycle process through the use of computer control technology.

SESSION 22

AIR QUALITY AND EMISSION TRENDS

Chairman: R.E. Neligan
Environmental Protection Agency

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THE IMPACT OF EMISSIONS CONTROL TECHNOLOGY ON PASSENGER CAR HYDROCARBON EMISSION RATES AND PATTERNS

F. Black*

ABSTRACT

A brief history of the regulation of passenger car hydrocarbon emissions, including the control systems and devices utilized for emission reduction, is presented. Three types of emissions are discussed: crankcase ventilation, evaporative gasoline, and combustion exhaust. Only exhaust and evaporative emissions are of significance and detailed hydrocarbon patterns for these are presented.

A variety of configurations have been employed by motor vehicle manufacturers for reduction of exhaust hydrocarbon emissions and the degree of control of specific hydrocarbons or groups of hydrocarbons is variable with the control system. Hydrocarbon emission patterns are presented as a function of control system for a variety of catalyst and noncatalyst vehicles. Increase in emissions with vehicle aging is also discussed.

INTRODUCTION

Sources of hydrocarbon emission into the environment are numerous and widely variant. Many estimates of the relative significance of the varied sources have been made in recent years and all involve many assumptions. It was determined, however, that the motor vehicle was a very significant source warranting control.

Through authority granted in the Clean Air Act of 1967 and the 1970 Amendments, the U.S. Federal Government promulgated a schedule for reduction of emissions of hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x) from new motor vehicles. The schedule was ambitious, calling for very dramatic decreases in emissions.

This presentation discusses the effect of this regulatory action on the emission of hydrocarbons into the environment from gasoline powered passenger cars which account for in excess of 80 percent of the motor vehicles in this country. Several engineering approaches to emission control are discussed including varied catalyst and non-catalyst systems. Both changes in mass and patterns of hydrocarbon emissions have resulted from application of these systems and are discussed.

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* Environmental Protection Agency, Research Triangle Park, North Carolina.

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EMISSION TRENDS

In 1971, the National Petroleum Council projected decreases in annual emissions from motor vehicles as shown in Figure 1 (1). These estimates were based on emission rates predicted using the 1968 Federal Test Procedure and the promulgated schedule of emissions reduction. The current test procedure would increase these estimates, but the trends illustrated are valid. The currently utilized urban driving simulation and analytical procedures are considered more accurate than those used previously. One must be careful when evaluating historical data. Driving patterns typically used in vehicle testing have been changed and these changes affect the emissions significantly.

Table 1 illustrates the magnitude of control called for by the legislation.

TABLE 1. EXHAUST EMISSION REDUCTION

	Hydrocarbons,		Carbon Monoxide,		NOx	
	g/mi.	g/km.	g/mi.	g/km.	g/mi.	g/km.
Pre-1968 vehicles (uncontrolled)*	9.1	5.7	97	60.2	3.34	2.07
Statutory levels (highest degree of control called for)	0.41	0.25	3.4	2.11	0.4	0.25
Percent reduction	95.5		96.5		89.1	

*low altitude, 49-state passenger cars (excluding California) (calender year 1976 values) (2).

The emission rates for uncontrolled vehicles were derived from actual tests with 320 vehicles, 1963-1967 model years, using the current Federal Test Procedure (2, 3).

Manufacturers responded to this call for reduction in emissions with many engine modifications and varied emission control packages. They have been effective in reducing emissions and, although not called for by law, many production engine groups are already emitting exhaust hydrocarbons at rates less than the statutory 0.41 g/mi level in low mileage vehicles.

In pre-emission control automobiles, there were three major areas of hydrocarbon emission: combustion exhaust, crankcase blowby, and evaporative loss from the fuel system. Table 2 illustrates the relative contributions of each.

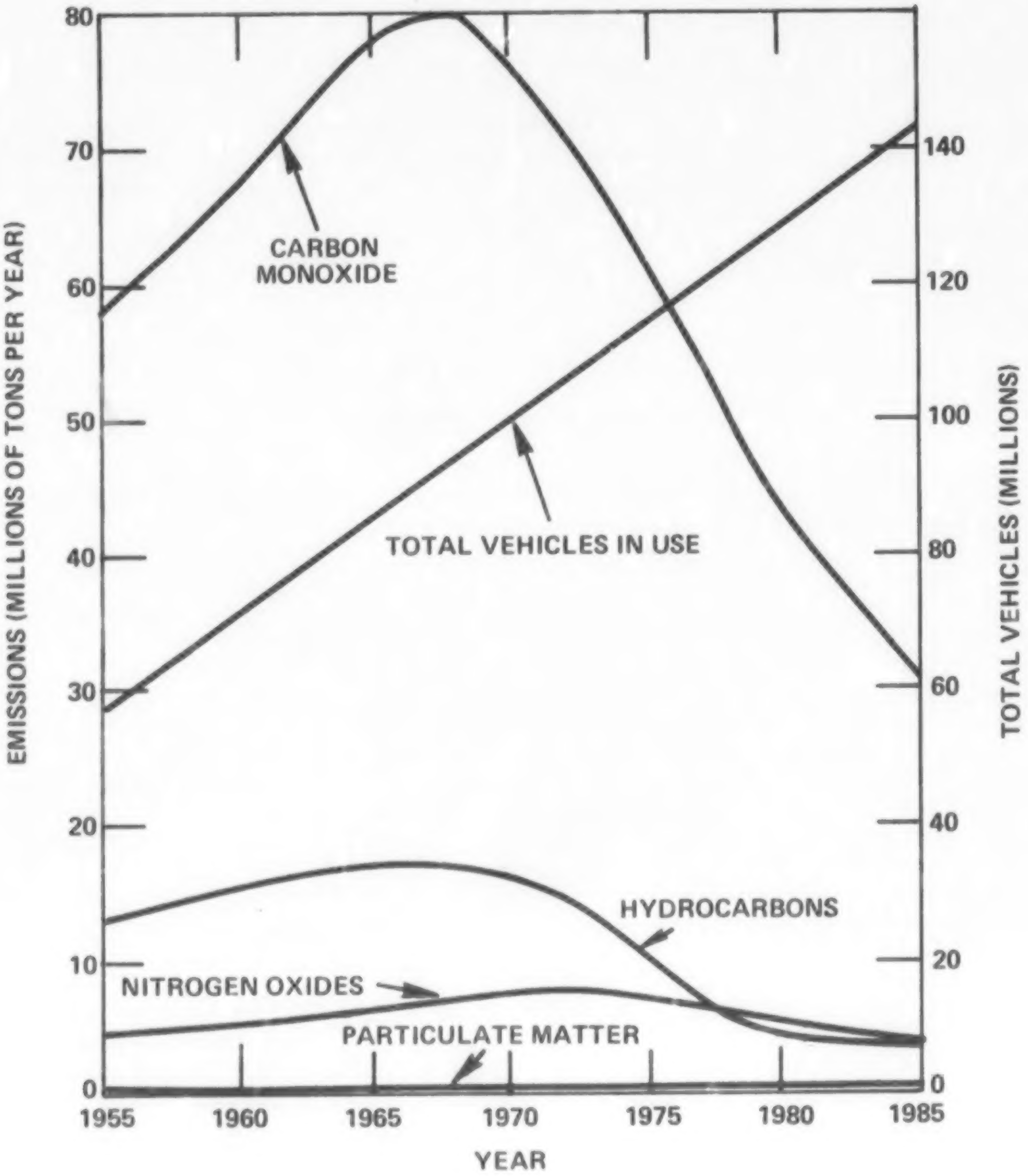

Figure 1. Mobile source annual emission rates (1).

CONTROL OF HYDROCARBON EMISSIONS

The advent of emission control has eliminated crankcase blowby emissions in low mileage cars, and exhaust hydrocarbons have been reduced greater than 95 percent for many vehicles. Crankcase blowby has been eliminated with Positive Crankcase Ventilation Systems. These systems provide for circulation of air through the crankcase and for drawing the circulated air and blowby gases into

TABLE 2. PASSENGER CAR HYDROCARBON EMISSIONS

	Exhaust		Blowby		Evaporative	
	g/mi.	g/km.	g/mi	g/km.	g/mi.	g/km.
Pre-control *	9.1	5.7	4.1	2.5	2.53	1.57
Percentage of total	57.9		26.1		16.0	

* Low altitude, 49-state passenger cars (2)

the intake manifold, where they are carried to the combustion chambers. The systems perform very well when maintained, but are subject to total failure if the critical control valve becomes clogged.

Engine modifications, catalytic converters, and combinations of both have been used to reduce exhaust emissions. Generally the engine modifications relative to exhaust hydrocarbon emissions permit operation on the lean side of the stoichiometric air-fuel ratio. Lean operation is attractive from an emissions standpoint as illustrated in Figure 2. Emissions of hydrocarbons (HC), CO and NO_x are favored by lean operation. Engine performance can suffer under lean operation, however, and most of the modifications are designed to maintain drivability throughout normal driving patterns. The catalyst systems are designed to complete combustion of the hydrocarbons emitted from the engine to CO_2 and H_2O prior to their being emitted from the tailpipe. This permits operations at air-fuel ratios favoring performance (12.5 best power, 15.7 best economy). The variety of catalyst systems employed is numerous and no attempt will be made to detail them. Hydrocarbon emission patterns from several systems are presented later in the discussion.

Evaporative emissions have been reduced by using adsorption-regeneration systems which use canisters of activated carbon to trap fuel tank and carburetor vapors and hold them until such time as they can be directed into the induction system for burning in the combustion chamber. These systems first appeared on motor vehicles in 1971. The standard of 2 g/test appeared to be easily met by the control systems utilized. The test procedure adopted by the federal certification laboratory (charcoal canister technique) (5), however, has been found to dramatically underestimate these emissions. More accurate procedures (Sealed Housing for Evaporative Determination, SHED, technique) (6) indicate actual emissions from post-control vehicles in the field to be near 12.0 g/test with about 12.1 g/day diurnal emissions (7). This equates to about 1.76 g/mi (1.09 g/km) (2). Ambient conditions (temperature and pressure) dramatically effect evaporative losses. Tests using the SHED technique with post-control vehicles in Denver gave 34.8 g/test with about 47.2 g/day diurnal (8). This equates to 5.51 g/mi (3.42 g/km). This is probably due to the lower atmospheric pressure and different fuel composition used in the Rocky Mountains. Exhaust hydrocarbon emissions are also somewhat higher at high altitudes.

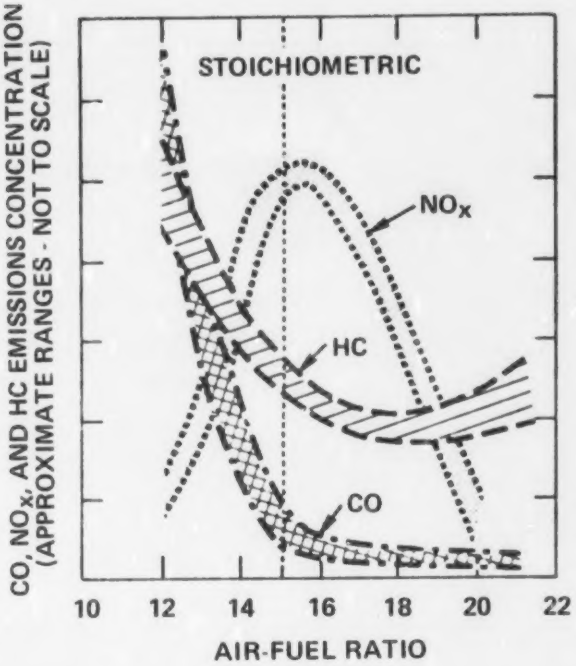

Figure 2. Effects of air-fuel ratio on exhaust composition (4).

Heywood effectively projected the significance of the higher than expected evaporative emissions on outyear aggregate emission rates as illustrated in Figure 3. The model used by Heywood assumes deterioration of the crankcase emission control systems as predicted by Voelz, et al. (9). It also assumes applicable exhaust standards are met during the life of the vehicle. The potential importance of evaporative emissions in outyears is readily apparent. The Environmental Protection Agency (EPA) is currently revising the evaporative emissions certification procedure to incorporate the SHED technique for the 1978 model year. Curve B is thus the most accurate prediction. It is based on 95% control in the 1977 model year, however, and this probably will not be realized until the 1978 model year.

Patterns of Hydrocarbon Emissions

Recognizing the relative contribution of exhaust, evaporative, and crankcase hydrocarbon emission, an examination of the detailed patterns of each ensues. The mass and pattern of hydrocarbons emitted from motor vehicles are dependent on many factors. The fuel; the emissions control system; the vehicle history (wear, deposits, vibration, and maintenance); ambient conditions (temperature, pressure, and humidity); and driving patterns are all significant controlling factors in vehicle emissions. Therefore, the conclusions of any reported study must be tied to the specific conditions under which the study was conducted. The trends indicated are generally true, but the absolute numerical quantities reported are of value only to indicate the trends.

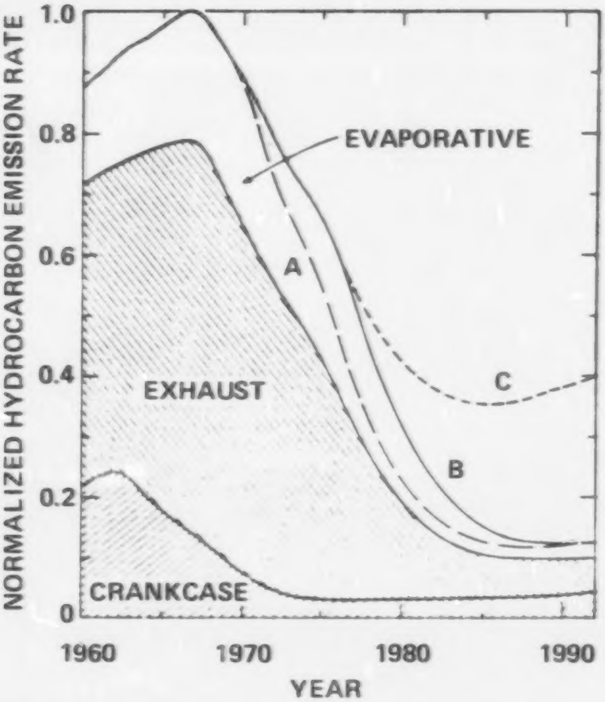

Figure 3. Normalized urban aggregate HC emission rate from in-use automobile population, baseline case. Crankcase, exhaust, and evaporative HC emissions indicated separately. Curve A-Conventional assumption that evaporative HC are 95% controlled in post-1970 vehicles. Curve B-Baseline-field data used to estimate HC evaporative emissions from 1971-1976 model year vehicles, with 95% effective control assumed in 1977 and subsequent model years. Curve C-Field data based estimate of evaporative HC used for all post-1970 vehicles. (8)

Tailpipe hydrocarbon emissions have been examined in some detail by gas chromatography (GC) for many new and older cars over the past several years in the EPA mobile source program at Research Triangle Park (RTP). The exhaust patterns to be discussed were determined for, generally, low mileage automobiles (<10,000 miles) tested with the 1975 Federal Test Procedure (FTP) (5). This procedure calls for driving the vehicle on a dynamometer over a defined urban driving cycle.

Table 3 presents the relative exhaust flow and hydrocarbon concentration of the modes under which vehicles are normally operated and the approximate percentages of the FTP driving cycle in each of these modes.

The hydrocarbon patterns reported below were determined using a consistent batch of lead-free gasoline the properties of which are shown in Table 4.

TABLE 3. EFFECT OF VEHICLE MODE ON HYDROCARBON EMISSIONS

Mode	Exhaust (10) Flow	Exhaust (10) HC Conc.	FTP Time in (8) Mode,%
Idle	very low	high	18.2
Cruise			
low speed	low	low	30.2*
high speed	high	very low	
Acceleration			
moderate	high	low	27.7
heavy	very high	moderate	
Deceleration	very low	very high	23.9

* The average speed of the 1975 FTP is 19.7 mph.

TABLE 4. FUEL USED FOR EXHAUST HYDROCARBON EMISSIONS TESTING

Research octane number	93.2
Motor octane number	84.7
Reid vapor pressure, psig	10.2
Distillation, ASTM D-86, °F	
10%	123
50%	199
95%	325
100%	383
FIA analysis, %	
aromatic	24.0
olefins	8.3
parafins	67.7

This fuel is reasonably representative of typically marketed lead-free gasoline The detailed hydrocarbon composition of the test fuel has been previously reported (11).

Tables 5a and 5b present the hydrocarbon exhaust emission patterns for a wide variety of catalyst and non-catalyst automobiles. Detailed GC procedures (12) were used to produce all listed data. The totals were based on summations of appropriate individual hydrocarbon concentrations.

TABLE 5a. AUTOMOBILE EXHAUST HYDROCARBON (AND ALDEHYDE) EMISSION PATTERNS

Vehicle	Control System	Total Exhaust Hydrocarbon, g/mi.	percentage of total hydrocarbon, wt.%								
			Methane	Paraffin	Acetylene	Benzene	Aromatic	Ethylene	Olefin	Formaldehyde	Tot. Aldehydes
1972 350 CID	non-catalyst	1.15	9.29	40.68	11.04	2,43	22.30	12.97	26.00	3.28	7.00
1974 Mazda rotary 40 CID	thermal reactor	1.47	8.99	41.62	6.20	2.04	18.04	17.45	33.70	6.83	11.00
1975 Ply. Fury 318 CID	single oxidation catalyst	.49	9.33	61.85	1.96	.88	18.87	5.29	17.25	1.10	2.20
1975 Ford Granada, 302 CID	single oxidation catalyst, air pump	.55	15.31	56.66	3.36	.73	19.49	7.60	20.47	-	-
1975 Chev. Impala, 350 CID	single oxidation catalyst	.25	15.44	57.09	2.72	1.44	19.68	8.76	20.44	1.60	3.64

TABLE 5b. AUTOMOBILE EXHAUST HYDROCARBON (AND ALDEHYDE) EMISSION PATTERNS

Vehicle	Control System	Total Exhaust Hydrocarbon, g/mi.	percentage of total hydrocarbon, wt.%								
			Methane	Paraffin	Acetylene	Benzene	Aromatic	Ethylene	Olefin	Formaldehyde	Tot. Aldehydes
Honda CVCC (proto.) 91 CID	Stratified Charge (lean)	.28	4.64	37.82	7.29	1.79	22.24	15.11	32.46	6.00	11.29
Chrysler (proto) 440 CID	electronic lean burn	.39	4.74	29.67	10.59	2.05	19.83	21.15	39.60	11.04	18.51
AMC Hornet (proto) 232 CID	dual bed reduction-oxidation catalyst	.31	24.97	78.15	1.23	.58	8.18	3.55	13.30	2.30	8.90
Volvo (proto) 130	three-way reduction-oxidation catalyst	.16	19.91	56.59	4.73	1.47	21.60	5.17	17.10	.94	3.25

In general, vehicles employing oxidation catalysts for exhaust hydrocarbon control have a lower percentage of unsaturated hydrocarbons than do vehicles without exhaust hydrocarbon control. Also, the methane percentage is increased. The net hydrocarbon photochemical reactivity is thus reduced. Of interest to those who use acetylene as a tracer for auto exhaust hydrocarbons in ambient air studies, the acetylene relative abundance in auto exhaust has been reduced significantly.

Four vehicle configurations of potential significance in outyear automobile populations are listed in Table 5b. The stratified charge engine, in which net lean combustion is used for emission control, yields a higher percentage of unsaturated hydrocarbons than previous non-catalyst cars. The Chrysler Corporation "lean-burn" engine also yields a higher percentage of unsaturated hydrocarbons. Two control systems are listed which are leading candidates for combined HC, CO, and NO_x control. Both the dual-bed and three-way catalyst systems yield lower percentages of exhaust unsaturated hydrocarbons than non-catalyst cars. This combined with the higher percentage yields of methane results in significantly lower net HC photochemical reactivity.

Exhaust aldehyde data are also listed. Here too, the percentage yields are lowest for vehicles employing catalysts for exhaust emission control. In general, the aldehyde rates are an order-of-magnitude lower than the hydrocarbon rates.

The detailed patterns of evaporative hydrocarbon emissions are dependent to a great extent on the gasoline used and ambient temperature and pressure. As previously mentioned, evaporative emissions are much greater in Denver than in Los Angeles, due primarily to the lower pressure and temperature of Denver and the attendent greater percentage of low molecular weight hydrocarbons in the fuel. This situation should be considered when attempting to define automobile sourced hydrocarbons in ambient air studies. In cities of higher altitudes the contribution of evaporative gasoline is greater. In the vehicle there are two primarily sources of evaporative losses: the fuel tank and the carburetor. The carburetor bowl potentially reaches higher temperatures and consequently the evaporative losses from this source reaches higher average molecular weight. The bowl total volume is also of significance to total mass of emission. The temperature, vapor volume, and pressure of the fuel tank are all of significance to tank losses. Many parameters impact the composition of evaporative losses, but in general it can be stated that the emissions are very much dominated by the C_4 to C_6 paraffins. Normal-butane and isopentane generally account for in excess of 50 percent of the total evaporative losses. Table 6 is representative of typical evaporative emissions. The dominance of n-butane and isopentane, and C_4-C_6 paraffins in general is readily apparent.

Crankcase blowby has been essentially eliminated with the positive crankcase ventilation systems. Voelz et al. estimated the systems to be about 98% effective (9). This estimate presumes proper maintenance of the system. In a study of over 75,000 vehicles in 15 metropolitan areas, 17 percent of the vehicles tested needed PCV system maintenance and 3.6% were emitting some crankcase fumes into the environment (9). The hydrocarbon composition of crankcase emissions is dominated by carbureted mixture (~85%) and combustion gases (~15%) (15,16,17). The patterns are thus very dependent on the fuel being used.

Lubricating oil does not contribute to crankcase emissions in a significant manner (18).

TABLE 6. PATTERNS OF EVAPORATIVE HYDROCARBONS

	Fraction of total evaporated hydrocarbons, vol. %	
	Carburetor (13)	Fuel tank (14)
Paraffins		
n-butane	11.9	30.5
isopentane	45.3	26.4
C_4-C_6	66.2	76.0
Olefins		
C_4-C_6	8.5	14.0
Aromatics		
C_6-C_7	1.0	1.3

The pattern of the aggregate hydrocarbon emissions from catalyst equipped vehicles is very much dominated by the paraffins. As discussed, this is due to the increased relative abundance of evaporative emissions with its paraffinic dominance and the greater activity of the catalyst for the exhaust unsaturated hydrocarbons. Table 7 is illustrative of the relative abundance of the various hydrocarbon classes.

For the purpose of illustration the 1975 Chevrolet Impala exhaust class weight percentages previously discussed were assumed to be typical of the model year. Also, it was assumed that 55% of the total evaporative emissions were from the carburetor and 45% from the fuel tank. About 75% of the aggregate emissions are paraffin, 9% aromatic, 15% olefin, and 1% acetylene. These estimated are for the 1975 model year. Outyear estimates vary as the relative abundance of exhaust to evaporative emissions changes. The 1975 model year emission factors suggest that the aggregate is composed of 41% exhaust, 59% evaporative (2). For the 1978 model year, the aggregate is estimated to be 35% exhaust, 65% evaporative (assumes exhaust standard is reduced to .41 g/mi).

Emission Control Systems Deterioration

Although mentioned, but not emphasized, deterioration factors are very important when attempting to assess the importance of the automobile to atmospheric pollution. Most of the data found in the literature is for low mileage (<10,000 miles) vehicles. With deterioration of emissions control systems, both hydrocarbon mass and patterns will change. Figure 4 is indicative of typical exhaust control deterioration factors. These factors are based on linear deterioration at the rate of 1 percent per year for the pre-1968 model years, 10 percent per year for the 1968-1974 model years, and 20 percent per year for the post 1974 model years (2). No inspection/maintenance program is assumed. Such programs would decrease the deterioration significantly. The factors for post-1974 model years were based on tests of prototype vehicles. The actual deterioriation factors for 1975 and later model year production vehicles should likewise be higher than 1968-74 model due to the increased sophistication of the control system, i.e. catalysts, air pumps etc.

The actual emissions increases experienced with post-1974 in-use vehicles on aging may be significantly different from that indicated by the published deterioration factors. The deterioration factors reported were determined with specific vehicles chosen for the durability fleet. They were maintained on owner's manual prescribed maintenance schedules and were not abused as consumer-owned vehicles might be. For example, these vehicles do not have their catalyst exposed to leaded gasoline, their carburetors are not tampered with to achieve better drivability, the spark advance is not set variant from manufacturers' specifications, and their catalysts are not physically removed from the exhaust system.

Ongoing surveillance programs are carried out by EPA under which consumer automobiles are tested and actual emissions from in-use vehicles are determined (19). Catalysts having been on automobiles for only two years, it is difficult to accurately project outyear emissions increases.

CONCLUSIONS

In conclusion, the advent of emission control has dramatically decreased the rate of emission of hydrocarbons into the environment from motor vehicles. Crankcase emissions have essentially been eliminated. Exhaust emissions have been reduced as much as 95% in some vehicles relative to uncontrolled vehicles. Vehicles using catalysts have seen a significant shift in the pattern of emissions with unsaturated hydrocarbons being reduced to a greater extent than saturated. The advanced catalyst systems also show significant increases in the relative abundance of methane in the exhaust. Vehicles using lean-combustion for emission control reduce saturated hydrocarbons to a greater extent than unsaturated hydrocarbon. Evaporative hydrocarbon emissions are dominated by the C_4-C_6 paraffins with n-butane and isopentane being the most significant.

In general, hydrocarbons emitted from outyear motor vehicles will show an increased dominance of paraffins due to the impact of catalyst on exhaust hydrocarbons and the increased relative abundance of evaporative hydrocarbons. The relative abundance of acetylene will decrease.

Ambient conditions significantly impact emissions. Hydrocarbon emissions are generally greater at high altitudes than at low altitudes, particularly evaporative emissions. Emissions will in general increase with vehicle age, potentially as much as a factor of three over ten years.

ACKNOWLEDGMENT

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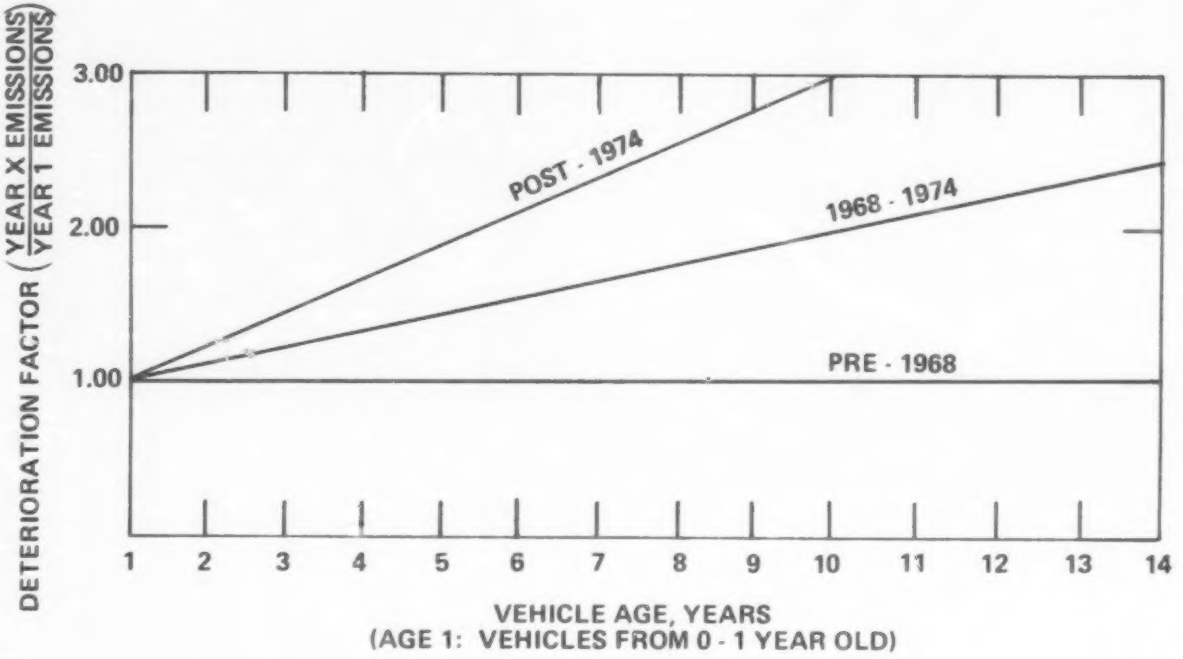

Figure 4. Exhaust hydrocarbon deterioration factors for light-duty gasoline powered vehicles (49-state cars).

TABLE 7. ESTIMATE OF COMPOSITE HYDROCARBON EMISSIONS FOR TYPICAL 1975 PASSENGER CAR *

	Exhaust	Evaporative	Composite
Total Hydrocarbon, g/km (2)	.75	1.09	1.84
Percent of total, wt.%	40.8	59.2	100
C_4-C_6 paraffins, wt.%	8.24	40.4	48.6
Olefin, wt.%	8.34	6.67	15.0
Aromatic, wt.%	8.03	.66	8.7
Paraffin, wt.%	23.29	51.9	75.2
Acetylene, wt. %	1.11	-	1.1

*low altitude 49-state car

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CONTROL OF OXIDANTS IN SYDNEY

D. Iverach and M.G. Mowle*

ABSTRACT

The nature, extent and severity of photochemical pollution in Sydney are discussed. Recently observed health effects on school children have emphasized the seriousness of the problem.

Progress in combating the problem is reviewed. The importance of a cooperative investigation known as the Sydney Oxidant Study is stressed, The introduction of the U.S. 1973 vehicle emission standards is also discussed. Recent tests show that this standard will not bring about the reductions originally hoped for. For example, results of vehicle tests in Sydney show that exhaust hydrocarbon levels will only be reduced approximately 30% compared to more than 60% predicted on the basis of U.S. data. A revised emission inventory is presented taking these results into account.

Another disturbing recent finding is that polluted air from Sydney may be transported about 50 km to an area where considerable population growth is forecast to occur.

From all this it is clear that lower exhaust standards are needed to control the problem, but the nature of the vehicle industry in Australia will make the introduction of low, deterioration free emission technology a challenging task.

INTRODUCTION

With three million people living in an area of 1000 sq. km., Sydney is Australia's largest city. Located on the east coast of the continent at latitude 34°S, the city lies across the east-facing mouth of the Parramatta River basin. Gently rising hills lie to the south, west, and north of the region. Westward the land continues to rise and 90 km from the coast the hills are about 1200 m high.

In this region the use of 1.2 million motor vehicles combined with the operations of an extensive range of industries result in the emission of more than 400 tons/day of hydrocarbons (HC) and about 170 tons/day of nitrogen

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oxides (NO_x). It is not surprising therefore that photochemical oxidants form in undesirable amounts whenever appropriate meteorological conditions prevail.

The problem of photochemical pollution first came into prominence in Sydney in November 1971 when widespread damage to petunia seedlings was identified as being caused by oxidants. Full realization of the seriousness of the problem came in March 1976 when thirteen school children were taken to the hospital after suffering from chest pains and breathing difficulties while exercizing. The symptoms have been attributed to oxidants; at the time of the incident ozone (O_3) concentrations over 0.2 ppm were recorded in the vicinity of the school. Prior to this occurrence the main recorded effects of oxidants had been vegetation damage, reduced visibility and accelerated rubber cracking. Few reports of eye irritation had been received.

To put the problem in perspective it should be added that the potential for a Los Angeles scale problem does not exist in Sydney. It is not likely that hourly values as high as those measured in the Los Angeles basin (up to 0.7 ppm) could form in Sydney. Perhaps more pertinent is the fact that meteorological conditions are such that Sydney should never experience the same frequency of high levels as recorded in that city (150 days per year over 0.15 ppm).

Typically in Sydney there are five to ten episodes per year, each lasting one to five days when O_3 concentrations in excess of 0.15 ppm (1 hr ave) are measured. Hourly values over 0.25 ppm and peaks over 0.4 ppm have been recorded infrequently.

If nothing were to be done, 0.15 values would become 0.25 within a decade and such values might occur on 20-30 days each year. Although not compatible to experiences in Los Angeles, such a situation would, on present day attitudes, be considered a very serious one. Indeed there is considerable concern about the existing levels. Fortunately the need for effective action has been recognized.

PROGRESS TO DATE

In 1971 when oxidant pollution was first recognized as a problem, very few data existed on which to base a control strategy. The extent of the problem was not known; virtually nothing was known of the concentrations of the precursors, reactive HC's and NO_x; the important role of meteorology was only suspected, and no emissions inventory was available. Nor was there provision in the Clean Air Act to regulate vehicle emissions.

Progress in both data collection and analysis and in the legislative areas has been substantial, but as is the case in the rest of the world, much remains to be done.

With respect to data collection and analysis, perhaps the single most important decision the commission has made was to enlist the aid of three external organizations. It is not common in Australia for a State Government Department to contract outside organizations in the scientific area. However, the study of oxidants in Sydney required a greater variety of measurements to be made with more sophistication than had hitherto been attempted. Contracts have been entered into with specific groups within the University of Sydney, Maquarie University and the Commonwealth Scientific and Industrial Research Organization (CSIRO).

At the same time, the Commission has increased its staff and developed its facilities in order that it be still directly involved in the day to day effort and not simply a contract manager or coordinator. Approaching the problem in this way allowed a much greater effort to be mounted more rapidly than would have been possible by doing all the work in-house, but without losing the essential information that derives from day to day involvement.

The responsibilities and interests of the four groups are listed below. The activities in parentheses are not financially supported by the Commission but obviously contribute to the study.

- The State Pollution Control Commission – Coordination, development of control strategies, development of emission inventories, responsibility for fixed site monitoring and mobile monitoring, including use of ground, sea and air craft.
- The University of Sydney – Responsibility for ground based mobile monitoring along air mass trajectories, analyses of data and determination of driving conditions in Sydney (development of p.c. smog models for Sydney and development of emission inventories).
- Maquarie University – Responsibility for meteorological measurements and analysis of wind data and air movements (development of models).
- CSIRO – Responsibility for detailed measurements of reactive HC's and development of a doubly compartmented smog chamber (measurement and analysis of aerosols).

Published results from the various groups are listed in the reference section.

With respect to legislative developments, the most significant event was the decision in November 1972 by the N.S.W. Government to amend the Clean Air Act to provide for the regulation of vehicle emissions. Regulations were gazetted in April, 1974 requiring, among other things, control of evaporative emissions on new cars manufactured after 1 January 1975 and the U.S. 1973 exhaust emission standards to be met on new cars manufactured after 1 July 1976. This action had been proposed in 1972. Details of the development of this and other vehicle related legislation and the anticipated effects may be found in Murphy (1975) and Iverach and Bilger (1975).

The important decision to adopt the U.S. 1973 standards and test procedures was based primarily on practical considerations.

It has been pointed out that lack of data made it difficult to develop a control strategy in the early years of the problem. However certain qualitative judgements could be (and were) made. If the automobile were the major emitter of precursors in Los Angeles there were good reasons to suspect this to be the case also in Sydney. On a per capita basis vehicle ownership and usage were somewhat comparable but there were fewer other major sources of oxidant precursors (oil refineries and power stations) in the Sydney region. Emissions of HC and NO_x from vehicles had to be significant. This was verified by emission inventory calculations which, when calculated on a two by two mile grid square basis, also allowed non-methane hydrocarbons (NMHC) and NO_x concentrations to be predicted. It was then possible to compare these predicted concentrations with the various oxidant NMHC NO_x relationships that had been developed. These relationships had been used in the U.S. and Japan to determine whether HC or NO_x should be controlled preferentially.

Iverach (1975) summarizes the situation. Neither an HC only (U.S. approach) nor an NO_x only (Japanese approach at that time, 1973) strategy was unmistakably indicated. This suggested concentrating on HC control because the technology for it was better developed both for mobile and stationary sources. Hence, adaptation of the U.S. 1973 standards was consistent with both the strategy as it could be derived at the time and the philosophy of using the "best practicable means" to control pollutants.

Using a "best practicable means" approach to the problem rather than promulgating what may have been impossible, though justifiable, is typical of pollution control in Australia and has been used since the first Clean Air Acts were gazetted in the early 1960's. Such an approach does not promise that the lowest possible emissions will be attained but neither does it threaten to involve the Government in a "back-off" situation as has occurred recently in the U.S. and Japan. Perhaps the main disadvantage of the approach is that it does not force, or at least encourage, the development of control technology.

RECENT DEVELOPMENTS AND FUTURE OPTIONS

A deal of data have been gathered since smog was first recognized as a problem in Sydney and more will be obtained in the near future. The most significant developments are summarized below.

EMISSIONS INVENTORY

The emissions inventory for HC and NO_x continues to become more accurate as actual measurements of sources replace emission estimates that were based on the U.S. Environmental Protection Agency (EPA) emission factors. Significant differences have been found between the EPA factors and actual emissions in Australia. For example NO_x emissions from stationary sources have been found to be approximately one-half the EPA factors. Preliminary measurements of pre-1977 vehicle emissions have indicated average exhaust HC emission rates of about one-half the pre-1968 U.S. model (uncontrolled) value. NO_x emission rates are about 15-20% higher than pre-1968 vehicles in the U.S.

Although evaporative emissions have not been measured in Australia using the SHED method the recent discovery in the U.S. of high evaporative emissions from "controlled" vehicles will most likely carry over to Australia because identical control techniques have been used. This has caused a further revision in the estimates of the benefits of existing controls.

Current estimates of emissions from vehicles in Sydney compared to U.S. data and U.S. 73 standards are shown in Table 1.

The present best estimates of Sydney's emissions are summarized in Table 2. Estimates for 1971 are shown in parentheses. Most of these estimates should be given 'B' or 'C' rating in terms of AP42 (EPA, 1975).

TABLE I. VEHICLE EXHAUST EMISSIONS

Vehicle Fleet or Standard	Emissions CO	g/Km HC	NOx
Ave. of 81 Sydney Vehicles tested in 1976	32	3.0	2.6
Uncontrolled U.S. (pre 68)	54	5.5	2.25
U.S. 1973 Standard	24.2	2.1	1.9

PRECURSOR MEASUREMENTS

Much effort has gone into measuring early morning concentrations of reactive HC and NO_x. The detailed results may be found in Allen et al. (1976). In general it has been found that $NMHC/NO_x$ values are in reasonable agreement with values predicted from the present emission inventory. In addition, concentrations are rarely measured that are as high as the 'worst case' predictions made by Iverach et al. (1976). High oxidant day precursor concentrations are 0.02-0.15 ppm NO_x and 0.2-1.5 ppm NMHC. Perhaps most importantly, precursor concentrations have been related to oxidant levels downwind on several occasions, and fair agreement has been found with currently accepted oxidant-precursor relationships.

AIR MASS TRAJECTORIES

Hyde and Hawke (1976) describe the various kinds of meteorological conditions that prevail on high oxidant days. Their most important conclusion, based on modelling air mass trajectories, is that on a high proportion of high oxidant days photochemical oxidants may be transported some 50 km. to the south west of Sydney – an area where considerable population growth is anticipated.

TABLE 2. EMISSIONS OF NON-METHANE HYDROCARBONS AND NO_x IN SYDNEY (TONNES/DAY), 1976 AND (1971)

Source	Hydrocarbons		NO_x	
Light Duty				
Vehicle-Exhaust	110	(176)	103	(86)
Vehicle-Evap.	63	(51)	-	
Vehicle-C' case	10	(39)	-	
Petrol Trucks, all sources	18	(11)	8	(6)
Diesel Truck	1	(1)	13	(10)
Motor Cycles	14	(12)	-	
Utility Engines	16	(13)	-	
Air, Rail & Shipping	3	(3)	4	(3)
Total Mobile	235	(306)	128	(90)
Industrial Combustion	8	(7)	33	(58)
Incineration	9	(7)	1	(2)
Refineries	53	(45)	7	(13)
Storage, Transfer of Gasoline	21	(18)	-	
Solvent Evap.	67	(56)	-	
Service Stns.	14	(12)	-	
Dry Cleaning	10	(8)	-	
Total Stationary	173	(152)	41	(72)
Grand Total	418	(458)	170	(161)

FUTURE CONTROLS

Future control will focus on vehicles, the refineries and associated gasoline transfer operations that exist to serve the needs of motorists, and on solvents. This discussion presumes that relatively straight-forward steps such as legislation of the Rule 66 type can be taken to reduce the importance of solvent emissions. Achieving significant reductions in vehicle emissions, however, is likely to be tougher.

The total Australian market is relatively small – about 600,000 units/yr. The N.S.W. market is about 200,000 (170,000 cars and station wagons). This market is split between some twenty-five companies offering some 150 models. The local manufacturers, General Motors-Holden, Ford (Aust), Chrysler Australia, and Leyland (small) have the largest share of the market but have lost ground in recent years to Japanese imports (mainly Toyota, Datsun, Mazda and Honda). The top ten companies achieve about 98% of sales in the light duty vehicle market.

Some automobiles are manufactured in Australia; some producers simply import the assembled vehicle but may have to install seatbelts or, as happened in NSW, evaporative emission controls, depending on local regulations and the ability of the overseas principal to comply with them.

All companies rely heavily on their overseas principals for emission control system design. Even local manufacturers have only limited design authority. The importers and assemblers rely absolutely on their overseas companies for virtually all emission control work. And to reiterate: often the Australian (and N.S.W.) market accounts for only a small fraction of their total sales. Consequently many of the companies are slow to adapt and react to new standards. Few are actively pursuing new engine designs or modifications in anticipation of future standards. Indeed only the local manufacturers and the local carburetor manufacturer (Bendix Corp.) have emission testing facilities in Australia and these are located in their development laboratories. Only Leyland of all the vehicle companies has an emission test facility in N.S.W.

Despite these difficulties this industry has to be persuaded, in some manner, to adopt what preferably should be a new, low emission, technology. It must be a new technology because, even assuming evaporative emissions can be properly controlled, the need for exhaust emissions substantially lower than the current standards can be demonstrated. And it is most important that essentially non-deteriorating technology be used. The use of technologies or techniques that suffer the currently observed rates of deterioration (EPA, 1975 and Stork, 1976) will not allow even modest improvements to be made in air quality.

The only technologies that offer real hope in this regard are the diesel and the stratified charge engine. Both these technologies are new to the mass-produced light duty vehicle scene. However, influencing the adoption of these and possibly other, yet to emerge, engines is one of the great challenges facing governments in Australia today.

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OXIDANT AND PRECURSOR TRENDS IN THE METROPOLITAN LOS ANGELES REGION

J. Trijonis, T. Peng, G. McRae, L. Lees*

ABSTRACT

This paper describes recent historical trends in oxidant and precursors in the Los Angeles region. Control strategies and basin-wide emission trends for nitrogen oxides and reactive hydrocarbons are documented year by year from 1965 to 1974. Trends in the geographic distribution of emissions are illustrated by computing net percentage emission changes over the decade for individual counties. The changes in emissions are compared to changes in ambient precursor concentrations and oxidant concentrations. It is found that many of the changes in monitored air quality can be explained by trends in total emissions and in the spatial distribution of emissions.

INTRODUCTION

The control of photochemical oxidant is a complex, dynamic process involving major technical uncertainties. An effective way to deal with the dynamic and uncertain aspects of the problem is to adopt a "feedback" approach in control strategy planning. Progress (or lack of progress) in improving ambient air quality should be continually reviewed. Control strategies should be periodically reexamined and, if necessary, reformulated. Control plans should be flexible so that changes can be made as new information is developed.

Trend analysis constitutes a fundamental part of the feedback approach to air pollution control. Air quality and emission trends should be major factors in determining whether or not control strategies need reformulation. Trend studies also can help to reduce technical uncertainties. For instance, the analysis of ambient precursor trends can indicate the adequacies, or deficiencies, in emission inventories and emission reduction estimates. Comparing historical oxidant changes to precursor emission changes can provide insight into the relationship between emissions and air quality. This improved knowledge can be used in evaluating future control strategies.

This paper documents trends for oxidant and the precursors (nitrogen oxides (NO_X) and reactive hydrocarbons (HC)) in the Los Angeles region from 1965 to 1974. Changes in basinwide precursor emissions and in the geographic

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distribution of emissions are compared to changes in ambient precursor concentrations and ambient oxidant levels. Most of the results presented here are based on a recent report of the Caltech Environmental Quality Laboratory (1). The reader is referred to that report for detailed discussions of the methodology and results.

PRECURSOR EMISSION TRENDS

This section describes trends in control strategies and emissions over the last decade for the two oxidant precursors, NO_x and the reactive HC (RHC). The trend estimates are based on much of the latest information available for emission sources in the Los Angeles region. Included are new reactivity factors for HC emissions (2, 3), recent measurements of auto exhaust emission and deterioration factors (4, 5, 6, 7, 8), test data on the unexpectedly large contributions made by evaporative emissions from light-duty vehicles (9, 10), the latest stationary source NO_x inventory (11), and recent data on traffic (VMT) growth and fuel usage patterns (12, 13, 14, 15, 16). A detailed description of the methodology for determining the emission trends can be found in Reference 1).

Basin-wide emissions of each pollutant are documented year by year from 1965 to 1974 in order to characterize overall emission trends and the changing role of various source categories. To illustrate the spatial distribution of emission trends, net percentage changes in emissions over the decade are determined for each of the six counties within (or partially within) the Metropolitan Los Angeles Air Quality Control Region (AQCR). Figure 1 shows the area covered by the Los Angeles air basin and the geography of the six county sub-areas.

TRENDS IN TOTAL EMISSIONS

The purpose of documenting basin-wide trends in total emissions is to help explain trends in average, basin-wide air quality. Total emission trends are also useful for illustrating changes in emission levels for various source categories. These changes result from emission control actions in competition with the growth of source activity levels. Since different source categories are associated with different rates of growth and degrees of control, the roles of various source categories have undergone continual alteration.

Figure 2 presents estimates of basin-wide NO_x emission trends over the past decade. The basin-wide total is represented by the top line, while the distances between the other lines illustrate the contributions of various source categories. Figure 2 shows that total NO_x emissions in the Metropolitan Los Angeles AQCR increased by about 36% from 1965 to 1974. The major contributor to this increase was the rise in NO_x emissions from light-duty vehicles; total NO_x emissions from light-duty vehicles increased by 75% over the decade. This was partially due to a 41% increase in basin-wide VMT and partially due to the large increase in NO_x emissions from 1966 – 1969 model year vehicles. The control techniques used to reduce HC and carbon monoxide (CO) in 1966 – 1969 vehicles had the side effects of raising NO_x emissions. New car emission

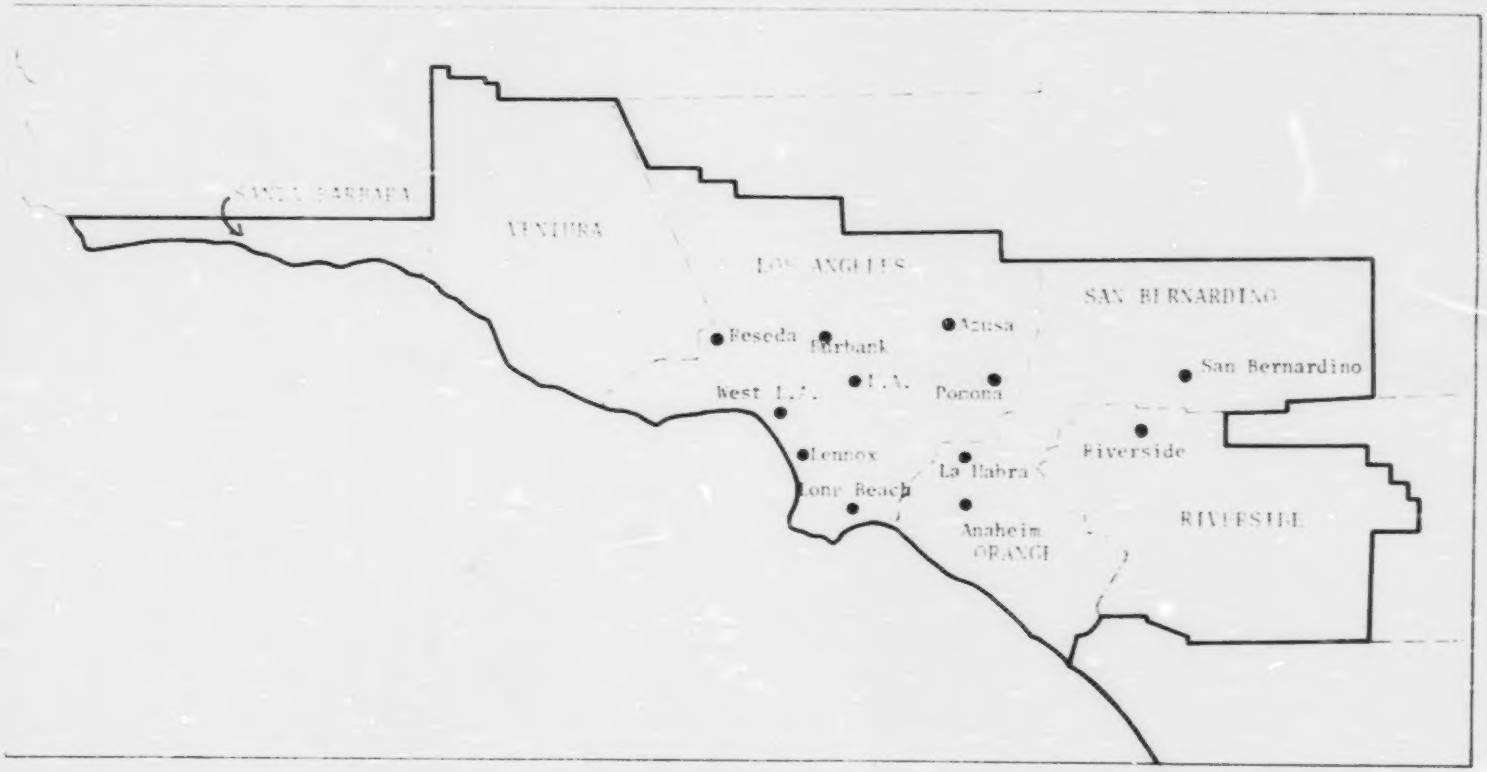

Figure 1. Map of the metropolitan Los Angeles AQCR.

standards for NO_x took effect in 1971, but as yet these standards have not had a great impact on basin-wide NO_x emissions.

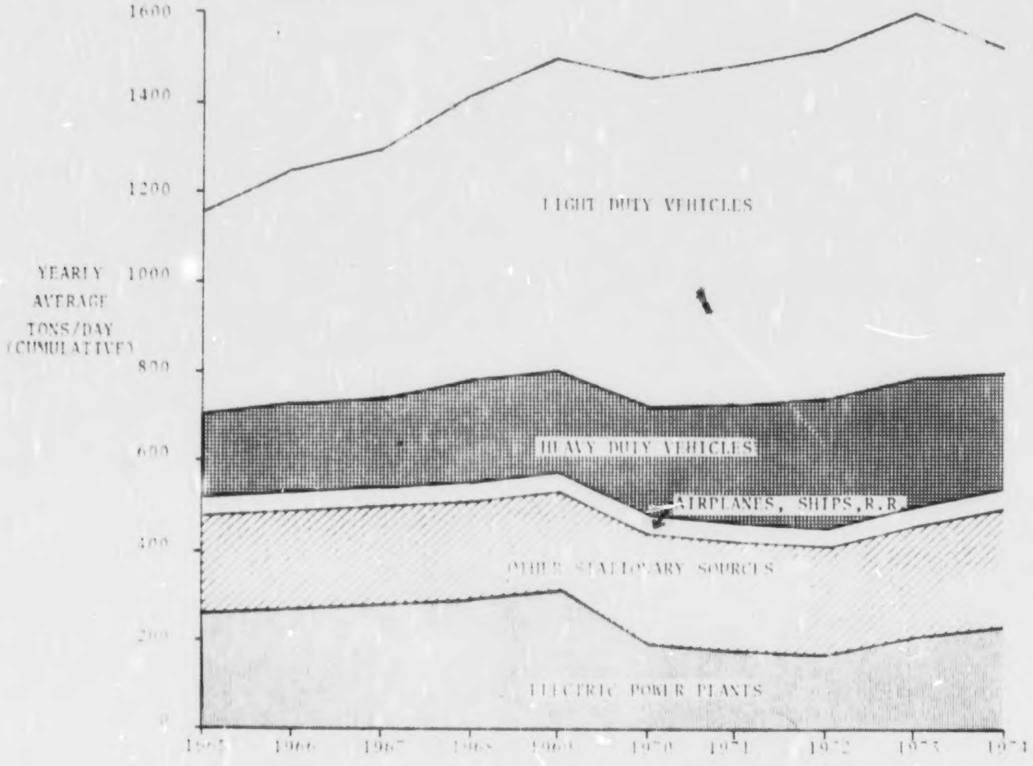

Figure 2. Total NO_x emission trends in the Los Angeles region.

Heavy-duty vehicles were also a growing source category for NO_x over the decade. Basin-wide emissions from heavy-duty vehicles increased by 40%, basically due to VMT growth. Although facing a high rate of demand growth, the electric power plants have contained and reduced their NO_x emissions effectively by use of natural gas and substitution of low-sulfur fuel for high-sulfur fuel in the sixties and by the Rule 68 retrofits and the industry's own extensive work which caused significant reductions after 1969. Nevertheless, the years 1972 – 1974 have already witnessed the growth of power plant NO_x emissions due to shortage of natural gas and increased use of fuel oil. Emissions from other stationary sources of NO_x essentially increased with energy use by those sources.

A slight downturn in total NO_x emissions occurred from 1973 to 1974. This downturn is partially due to emission controls on new light-duty vehicles, but it mainly reflects the energy crisis and resulting decrease in traffic from 1973 to 1974. The downward trend in total NO_x emissions should continue at an even greater rate after 1975 because of the stringent new car NO_x emission standards which started in 1975.

Figure 3 summarizes basin-wide trends in reactive HC emissions from 1965 to 1974. The top line represents total RHC emissions, and the distances between the lines represent the contributions from various source categories. Here, the definition of reactive hydrocarbon emissions is based on a two-group reactivity scheme proposed by Dimitriades (2) of the Environmental Protection Agency and on reactivity factors calculated in a recent TRW report (3).

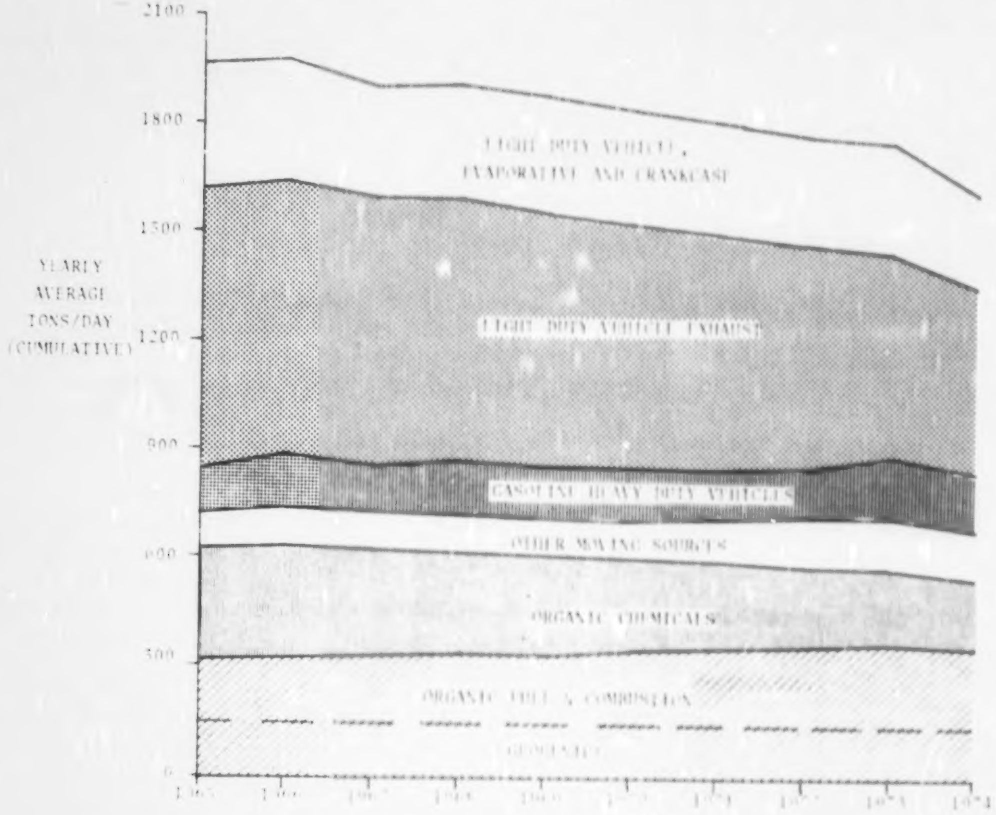

Figure 3. Total reactive hydrocarbon emission trends in the Los Angeles region.

The net change in basin-wide reactive hydrocarbon emissions over the decade was a decrease of 18%. Most of this reduction was due to controls on light-duty vehicles. Light-duty vehicle crankcase emissions were reduced in the early and middle 1960's. Slight reductions in evaporative emissions were obtained in the 1970's from the new car evaporative controls. Exhaust emission standards for new automobiles resulted in significant control of exhaust emissions. The net change in RHC emissions for the average vehicle over the decade was a 52% decrease. In the presence of a 41% increase in VMT, the net reduction in total RHC emissions from light-duty vehicles was only 32%.

Gasoline-powered, heavy-duty vehicles experienced a 23% reduction of per-mile RHC emissions over nine years, most of the reduction coming from crankcase emission control. With the 41% growth in VMT, the net change was a 7% increase over the period from heavy-duty vehicles. Emissions from other mobile sources have increased by 56%.

The organic chemicals category, the largest contributor of RHC in the stationary source category, has been reduced by approximately 33% from 1966 to 1974 due to APCD Rule 66 in the late 1960's and to substitution of water-based coatings for organic solvent coatings in the early 1970's. Emissions from gasoline marketing, which is a major source of organic fuel emissions, have increased by 26%, although filling of underground gasoline station tanks has been partially controlled by local APCD rules. An important part of the organic fuels and combustion category is the "geogenic source" that was recently pointed out by Mayrsohn and Crabtree (17). It is assumed that this source remained constant over the ten-year period.

GEOGRAPHICAL DISTRIBUTION OF EMISSION TRENDS

The spatial distribution of emissions, as well as the total amount of emissions, is important to ambient air quality. Accordingly, trends in the spatial distribution of emissions should be considered in analyzing air quality trends. This section illustrates large-scale trends in the geographic distribution of emissions within the Los Angeles air basin by documenting net emission changes over the decade on a county-by-county basis.

There is reason to expect that the spatial distribution of emission trends has been very nonuniform in the Los Angeles region. Although similar emission control policies apply to each county, growth rates vary considerably from county to county. Figure 4 illustrates the spatial pattern of VMT and population growth from 1965 to 1974. Growth rates for each individual county are presented within the boundaries of those counties, while basin-wide figures are given in the lower left-hand corner of the figure.

As indicated in Figure 4, the average VMT and population growth rates for the entire basin are 3.9% per year and 1.1% per year, respectively. Los Angeles County has been growing at a rate considerably slower than the other five counties within the basin. The fastest growing county, Orange County, has a VMT growth (7.5 percent per year) triple that of Los Angeles County (2.8 percent per year) and a population growth rate (4.3% per year) more than ten times that of Los Angeles county (0.3% per year). These differential growth rates, compounded year by year over the decade, led to a spreading out of emissions away from Los Angeles County to the outlying counties. Los Angeles County accounted for about 75% of basin-wide emissions of NO_x and RHC in 1965, but only for about 65% in 1974.

Figure 5 illustrates the spatial distribution of NO_x emission changes over the decade. The net percentage change in NO_x emissions over the decade is presented for each of the six counties and for the entire basin. Each county experienced an increase in NO_x emissions over the decade, with the basin-wide total increasing by 36%. Following the spatial trends in popula-

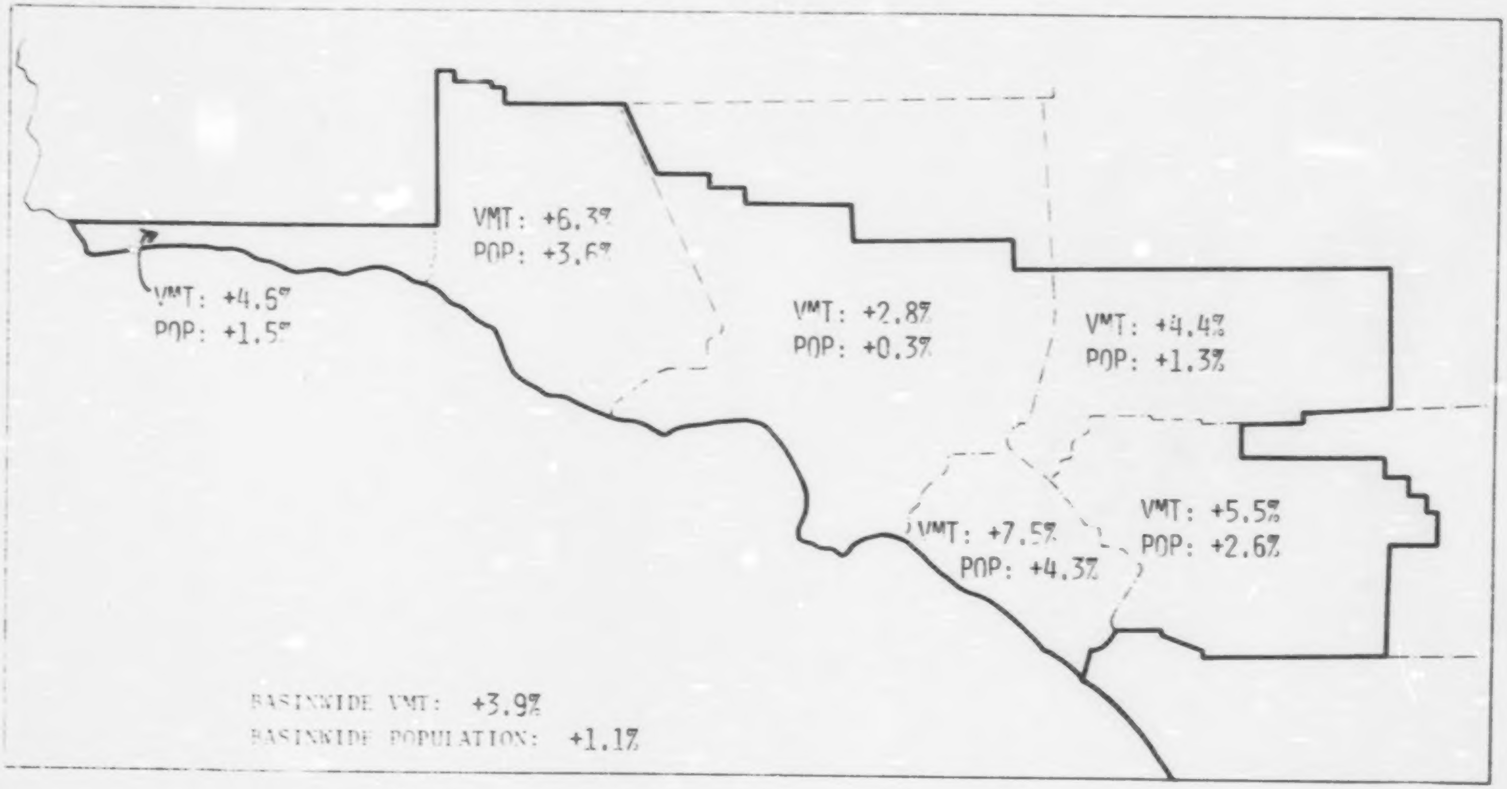

Figure 4. Average yearly VMT and population growth rates, 1965-1974.

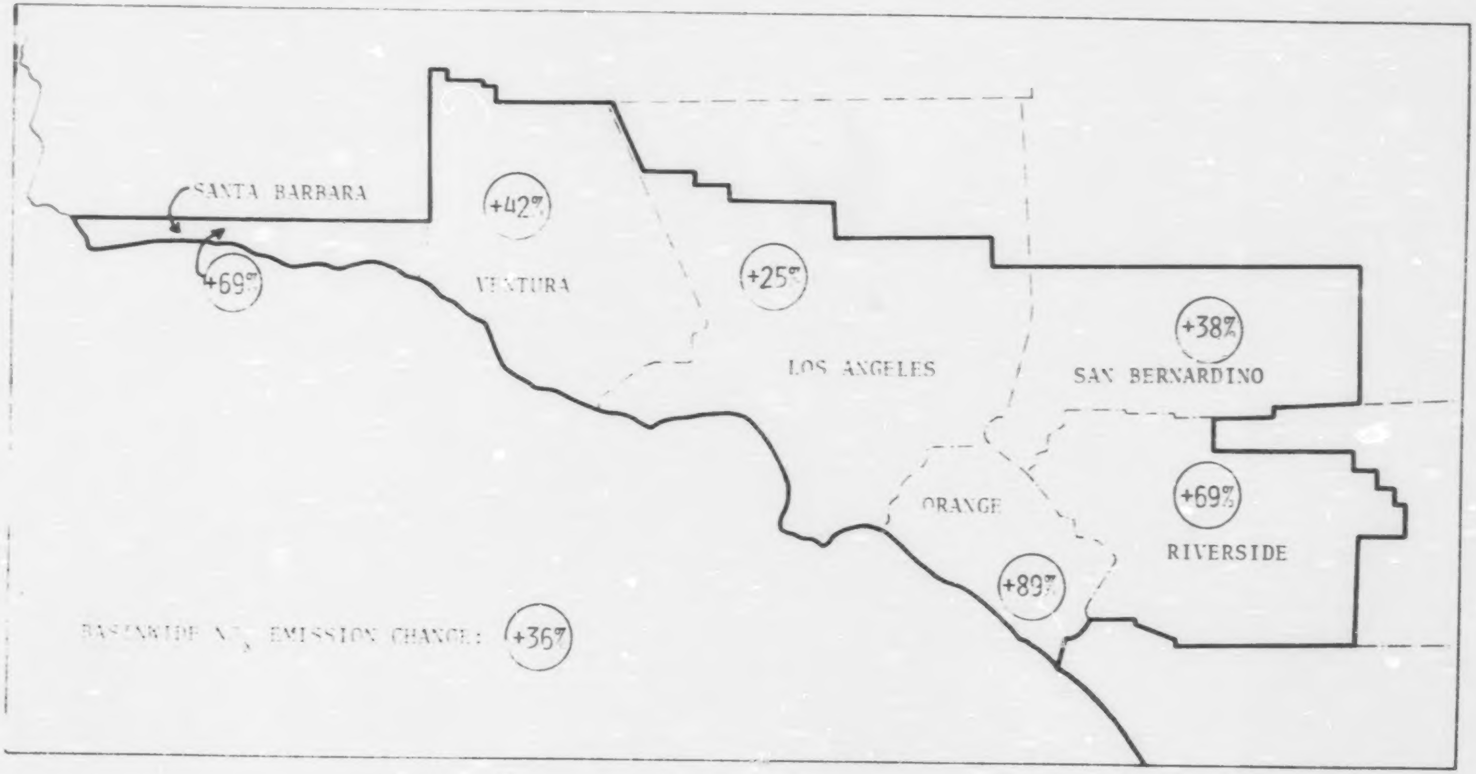

Figure 5. Trends in NO$_x$ emissions, 1965–1974.

tion and VMT growth, Los Angeles County NO_x emissions grew by the smallest amount, 25%. NO_x emissions in Orange County rose drastically, an estimated 89% increase over the decade.

Figure 6 presents the county-by-county distribution of RHC emission changes. Over the decade, basin-wide RHC emissions decreased 18%. Following the order of population and VMT growth rates, Los Angeles County showed the largest decrease, 24%, while the outlying counties experienced lesser decreases. In fact, Orange County evidently underwent an actual increase in RHC emissions of six percent over the decade.

AMBIENT AIR QUALITY TRENDS

Having documented emission trends in the Los Angeles region over the past decade, the next logical step is to compare the emission trends to air quality trends. This section presents air quality trends over the decade for both oxidant and its precursors and analyzes these trends in terms of the changes in total emissions and the spatial distribution of emissions. Comparing ambient precursor trends to emission trends provides a test of the adequacy of simple proportional (rollback) models for relating emissions and precursor concentrations. This juxtaposition also serves as a partial check on both the emission and air quality data bases. Comparing oxidant trends to precursor trends yields insight as to the oxidant/precursor relationship in various parts of the Los Angeles region.

The data base for determining air quality trends in the Los Angeles region consisted of computer tapes of hourly average pollutant measurements obtained from the California Air Resources Board (ARB). These tapes contained data from all stations in the Los Angeles region which reported to the ARB during the years 1963 to 1974. A search was conducted among personnel of the ARB and the County APCD's to determine whether monitoring changes occurred which could affect air quality trends. Data were included from each site only if they were taken with the same measurement method each year. It was determined that the locations of monitors in a few cities had been altered during the period of interest; data from these locations were eliminated from the study. Some of the monitoring sites that were included in the trend analysis are shown in Figure 1.

In order to compare air quality changes to emission changes over the decade, net changes in ambient concentrations were determined from 1965 to 1974. For each pollutant (NO_x, nonmethane hydrocarbons (NMHC), and oxidant), a least-squares trend line was fit to the yearly averages of daily maximum one-hour concentrations. The percentage change in this trend line from 1965 to 1974 was used as the measure of overall air quality change for each site. Yearly averages of daily maxima were eliminated from the analysis if the averages were based on a very limited number of sampling days. The analysis was performed only for stations with at least eight years of adequate data.

AMBIENT PRECURSOR TRENDS

Figure 7 compares changes in NO_x air quality to changes in NO_x emissions.

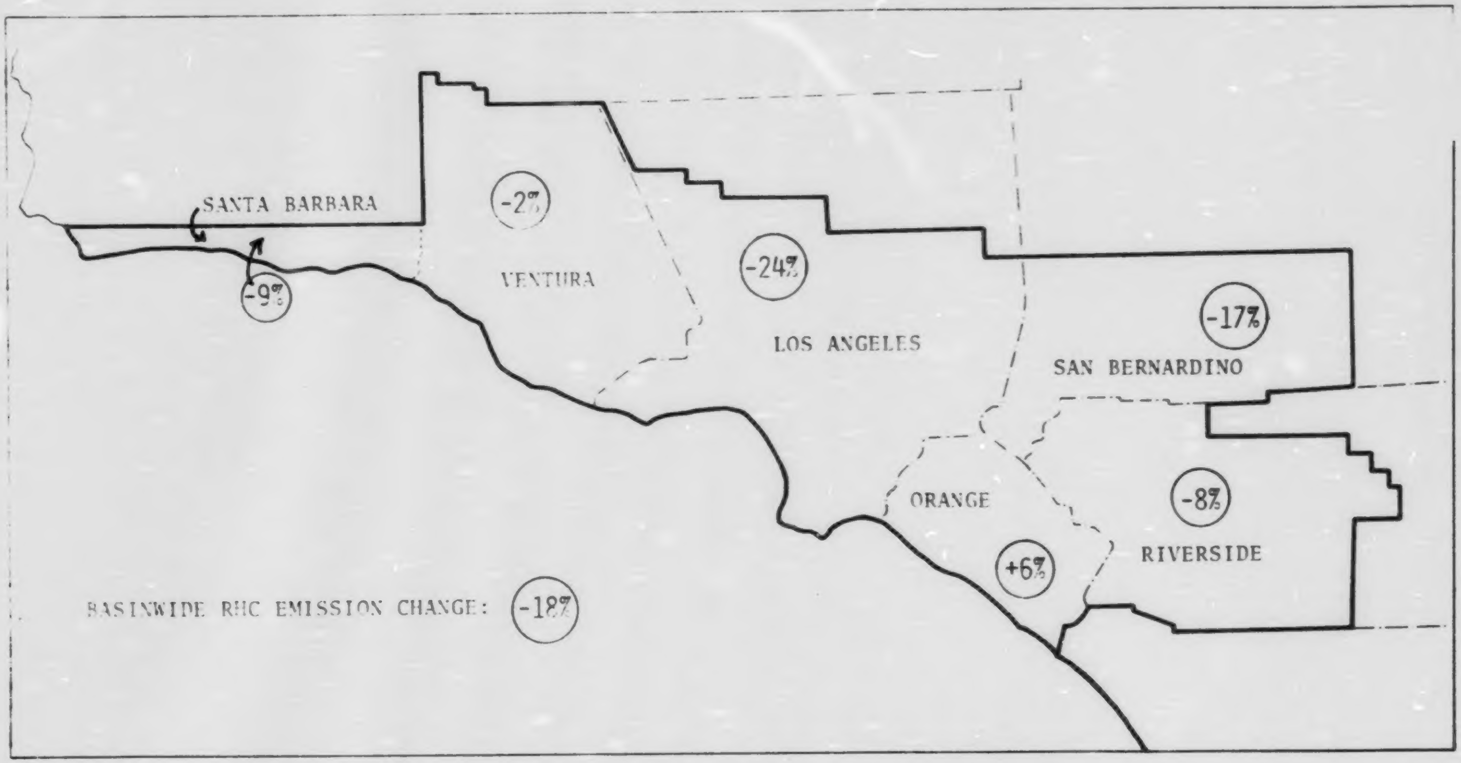

Figure 6. Trends in RHC emissions, 1965-1974.

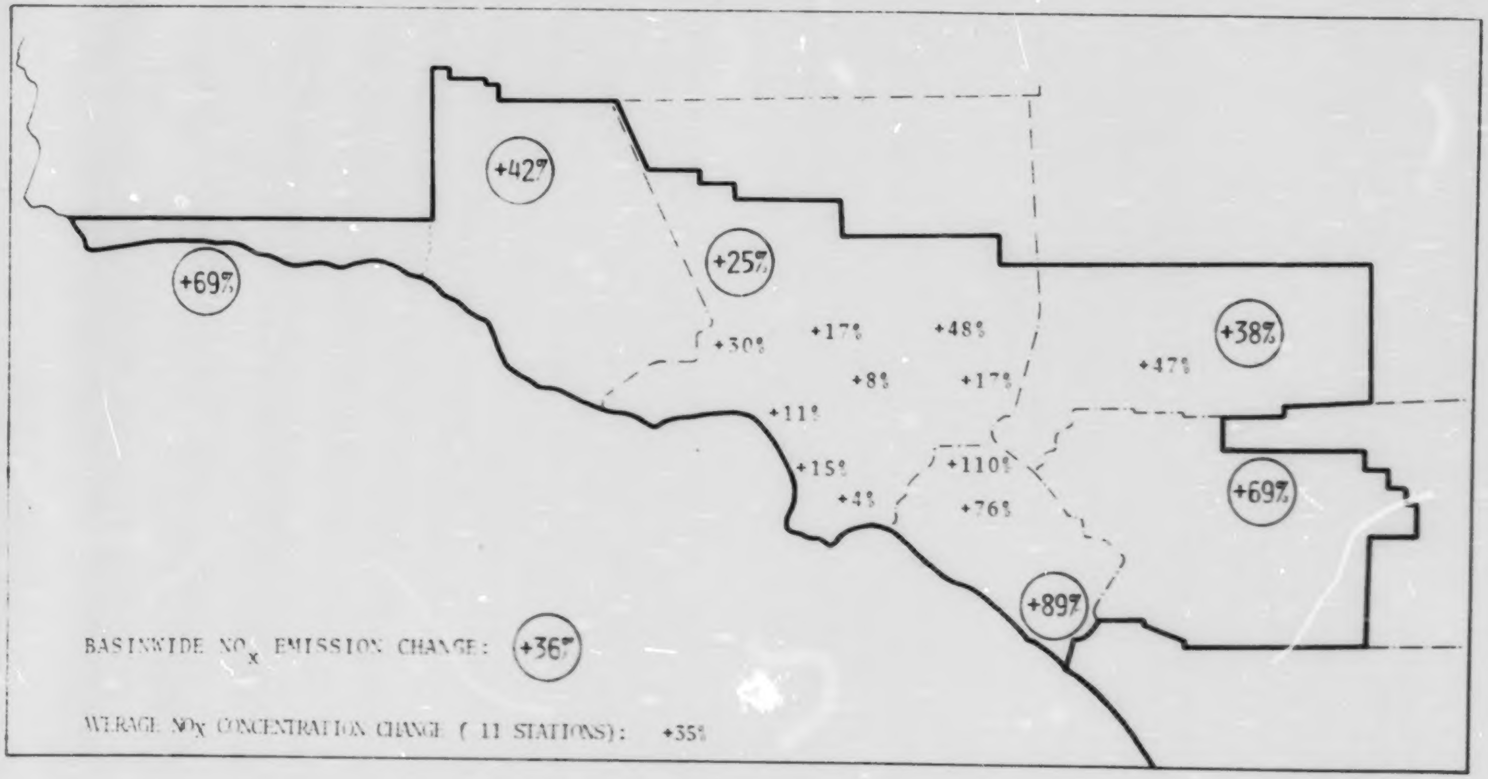
+42%
+69%
+25%
+30%
+17%
+48%
+38%
+47%
+8%
+17%
+11%
+15%
+110%
+4%
+76%
+69%
+89%
BASINWIDE NO_x EMISSION CHANGE: +36%
AVERAGE NO_x CONCENTRATION CHANGE (11 STATIONS): +35%

Figure 7. Trends in NO_x emissions and air quality, 1965-1974.

The circled numbers in Figure 7 represent the net percentage emission changes for each county over the decade (also given in Figure 5). For instance, Los Angeles County experienced a 25% increase in NO_x emissions over the decade; Orange County experienced an 89% increase; Riverside underwent a 69% increase, etc. The net percentage changes in ambient NO_x concentrations over the decade are also plotted in Figure 7 for eleven monitoring sites. For instance, ambient NO_x levels increased by 8% at downtown Los Angeles, 76% at Anaheim, 47% at San Bernandino, etc. Basin-wide averages in emission trends and ambient concentration trends are presented in the lower left-hand corner of Figure 7.

The agreement between calculated NO_x emissions changes and measured NO_x air quality changes is strikingly good. Total basin-wide NO_x emissions increased by 36% over the decade, while average NO_x concentrations at the eleven monitoring sites increased by 35%. Even the spatial distribution of emissions and air quality trends agree on a county-by-county basis. NO_x emissions grew by 89% in Orange County, while the two Orange County stations showed an ambient NO_x increase of 93%. NO_x emissions increased by 25% in Los Angeles County, while the eight Los Angeles County stations experienced a 19% increase in measured NO_x concentrations.

Figure 8 compares changes in NMHC concentrations to changes in RHC emissions. The circled numbers again represent net percentage emission changes, for each county and for the entire basin. Only four monitoring sites provide data sufficient for determining ambient HC trends. The net percentage changes in NMHC* levels over the decade are plotted at the locations of these four sites.

It is not possible to draw definitive conclusions concerning ambient NMHC trends because of the sparsity of sites providing data on changes in HC concentrations. However, it is encouraging that the average change in ambient NMHC concentrations among the four sites, a 15% decrease, is close to the basin-wide change in RHC emissions, an 18% decrease. Also, the spatial pattern of concentration changes seems to agree qualitatively with the spatial pattern of emission changes (at least in the sense that Los Angeles, San Bernandino, and Orange counties fall in the same order for concentration trends and emission trends). The only puzzling aspect of the ambient trend data for NMHC is the wide disparity between trends at the two sites in Los Angeles County, Downtown Los Angeles and Azusa.

TRENDS IN OXIDANT AIR QUALITY

Figure 9 illustrates percentage changes in oxidant concentrations over the past decade and compares these to changes in RHC emissions. The circled numbers represent RHC emission trends (county by county and basin-wide) while the other numbers represent trends in ambient oxidant levels at thirteen monitoring sites. Basin-wide, the agreement between RHC emission trends and oxidant trends is quite good; total RHC emissions decreased by 18% over the decade, while the average improvement in oxidant levels at thirteen stations was 19%. Also, the spatial distribution of air quality changes agrees quali-

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*Nonmethane hydrocarbon trends are computed from total hydrocarbon trends using empirical formulas relating THC to NMHC (18).

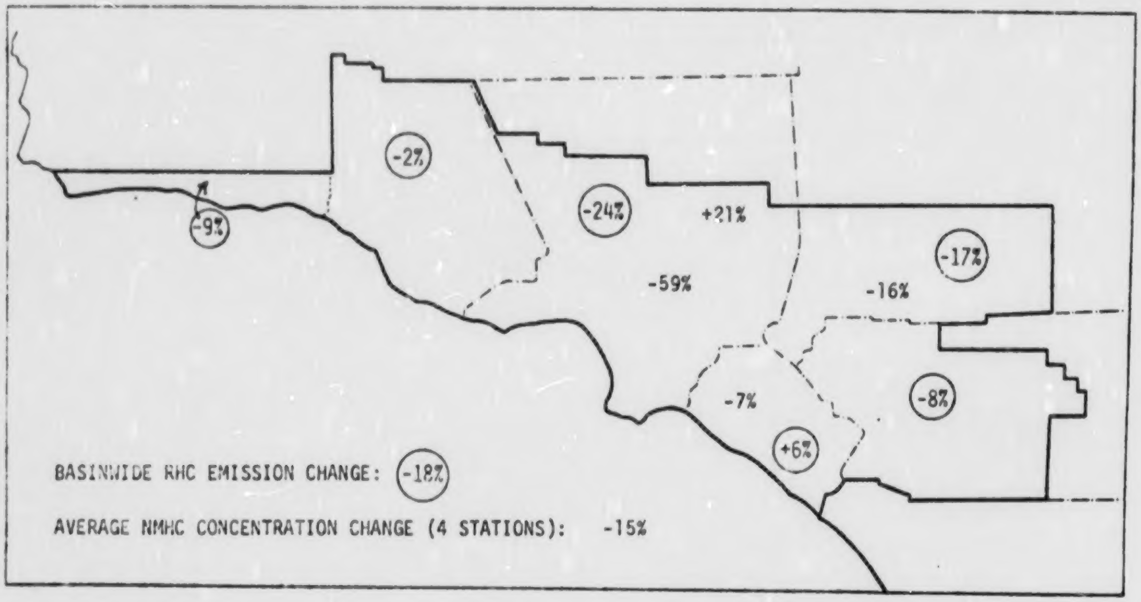
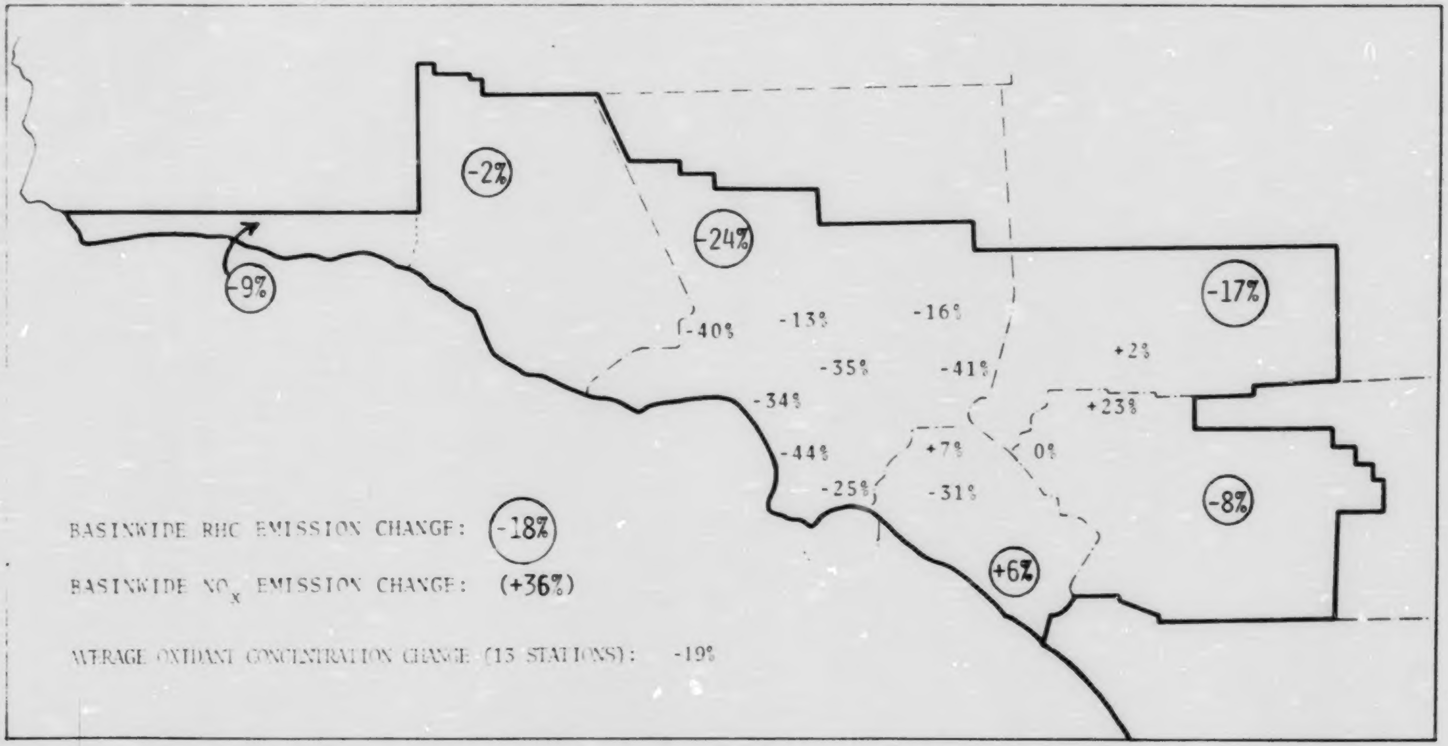

-2%
-9%
-24%
+21%
-59%
-17%
-16%
-7%
-8%
+6%
BASINWIDE RHC EMISSION CHANGE: -18%
AVERAGE NMHC CONCENTRATION CHANGE (4 STATIONS): -15%

Figure 8. Trends in RHC emissions and air quality, 1965-1974.

tatively with the spatial distribution of emission changes, at least in the sense that Los Angeles County experienced the greatest improvement in both RHC emissions and oxidant concentrations.

The spatial pattern of oxidant air quality trends can be even better explained by considering what has been termed the "dual role" of NO_x emissions in oxidant formation. From the present understanding of photochemistry, it can be argued that, at the existing ratio of RHC to NO_x, increases in NO_x emissions would tend to decrease oxidant concentrations in the source-intensive areas of the Basin (the central and western-coastal areas). In these areas, the highest oxidant concentrations occur early in the day (around noon) before the pollution is transported inland by the daily sea breeze. The most effective strategy for reducing oxidant near the source areas early in the day is to inhibit the reaction by reducing the RHC/NO_x ratio. This can be done by decreasing RHC emissions and/or increasing NO_x emissions. The transported oxidant problem in the eastern-inland areas should depend more on the absolute levels of RHC and NO_x than on the ratio. The key to controlling the transport problem is less understood, but indications are that reductions are needed in overall levels of RHC and (possibly) NO_x.

These observations help to explain why the coastal areas of Los Angeles County show the greatest improvement in oxidant concentrations (a 30 to 40% decrease from 1965 to 1974). These source-intensive areas have experienced a 24% decrease in RHC emissions, and they have been aided by the NO_x emission increase. The apparent anomaly at Anaheim, a 31% decrease in oxidant within a county with a 6% increase in RHC emissions, can be partially accounted for by the large NO_x emission increase (and resulting RHC/NO_x ratio decrease) at that source-intensive location. The lesser rates of improvement in the eastern-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+2%
-34%
+23%
-44%
+7%
0%
-25%
-31%
-8%
+6%
BASINWIDE RHC EMISSION CHANGE: -18%
BASINWIDE NO_x EMISSION CHANGE: (+36%)
AVERAGE OXIDANT CONCENTRATION CHANGE (13 STATIONS): -19%

Figure 9. Trends in RHC emissions and oxidant air quality, 1965-1974.

inland portions of the basin may be explained by noting that basin-wide RHC emissions have been reduced only slightly and that total NO_x emissions have increased. In particular, Riverside may have experienced a 23% increase in oxidant concentrations because it is downwind of Orange County, which had a 6% increase in RHC emissions and a large increase (89%) in NO_x emissions.

CONCLUSIONS

Basin-wide emissions of NO_x have increased by 36% in the Los Angeles region from 1965 to 1974, while basin-wide RHC emissions have decreased by 18%. Controls on crankcase and exhaust emissions from light-duty vehicles were largely responsible for the total RHC emission decrease. VMT growth and the increase in NO_x exhaust emissions from 1966 to 1969 model year vehicles were the major contributors to the total NO_x increase.

Projections of emissions made in the early 1970's (19) have turned out to be overly optimistic when compared to emission trends which we now determine in retrospect. The projections made in the early 1970's indicated a 20% increase in NO_x emissions and a 40% decrease in RHC emissions from 1965 to 1974. The error in the earlier projections is caused partly by the fact that test data for automobiles do not show as large emission reductions as would have been expected from the time-table of tightening emission standards. Evaporative emissions, for example, are much higher than called for by federal and state standards. For RHC, the new reactivity scale we are using now leads to a more pessimistic picture because it gives greater weight to source categories that have been reduced little in the last ten years. For NO_x, the shortage of natural gas for industrial interruptibles and power plants and the resultant unforeseen switch to fuel oil have produced higher emissions than originally projected for stationary sources. The occurrences of these unforeseen circumstances should serve as a warning in making future emission projections. A sensitivity analysis of air quality to the possible range of emissions should be included as part of future studies.

Emission trends reflect a competition between reductions from emission control and increases from source growth. Since the geographical distribution of source growth, in particular traffic growth, has been very nonuniform over the Los Angeles region, the geographical distribution of emission trends is also very nonuniform. Among the counties in the basin, Los Angeles County has grown the slowest, while Orange County has expanded at the greatest rate. This nonuniform spatial distribution of emission trends is important in interpreting air quality trends. What appear to be contradictory air quality trends at different locations in the basin can often be explained by the geographical distribution of emission trends. In analyzing future strategies, the geographical distribution of emission changes should be accounted for.

The basin-wide trend in ambient NO_x concentrations (about a 35% increase) agrees well with the basin-wide trend in NO_x emissions over the past decade (a 36% increase). The geographical distribution of NO_x emission trends and NO_x air quality trends on a county-by-county basis also agree. Ambient data on HC trends are very sparse. However, the average trend in NMHC concentrations at four locations (a 15% decrease) is consistent with the basin-wide change in RHC emissions (an 18% decrease).

The basin-wide improvement in oxidant air quality (19% over the decade) agrees well with the basin-wide reductions in RHC emissions. The geographical trends in oxidant agree, qualitatively, with the geographical trends in RHC emissions, especially for Los Angeles County. If we account for the dual role of NO_x we obtain an even better clarification of the geographical distribution of oxidant trends. The increase in NO_x emissions helped to decrease the RHC/NO_x ratio; this resulted in substantial oxidant reductions in the source-intensive, central-coastal areas. Little or no improvement in transport related oxidant occurred in the downwind, eastern-inland areas because overall RHC emissions were reduced only slightly and (possibly) because NO_x emissions increased.

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COMPARISON OF PAST AND PROJECTED TRENDS IN OXIDANT CONCENTRATIONS AND HYDROCARBON EMISSIONS

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ABSTRACT

Air quality projections for photochemical oxidants have been made for the years 1980, 1990 and 2000. These projections consider alternative levels of hydrocarbon control for mobile and stationary sources. In order to make the projections, assumptions concerning background concentrations and the hydrocarbon/oxidant relationship were necessary. These assumptions were tested using past trends in air quality and emissons. The projections indicate that for the most optimistic levels of control, significant improvements in air quality are projected for many areas within the United States. However, even with these improvements many of these same areas may not attain the National Ambient Air Quality Standard for oxidants by the year 2000.

INTRODUCTION

The U. S. Environmental Protection Agency (EPA) makes projections of photochemical oxidant concentrations in order to compare the effectiveness of proposed hydrocarbon (HC) control strategies. Recently an interagency task force on motor vehicle goals beyond 1980 analyzed the effect on air quality of different pollutant control strategies through the year 2000 (Tuerk 1976). One of the effects studied by the task force was the expected change in future year O_x quality.

Oxidant air quality projections were made utilizing two models relating HC emissions and O_x concentrations. These air quality projection models assume growth rates and future emission levels for both mobile and stationary sources. Uncertainties abound in the projections because of these assumptions. For photochemical oxidant projections, there are two additional uncertainties caused by inaccuracies in determining: (1) the proper relationship between HC emissions and ambient O_x concentrations, and (2) the appropriate background concentration for typical urban areas. These uncertainties are assessed by studying past trends in O_x air quality and estimated HC emissions. Finally, using the two air quality models, projections are made to the year 2000.

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TECHNIQUES FOR PROJECTING CONCENTRATIONS

AIR QUALITY MODELS

The effects of projected changes in HC emissions on O_x concentrations have been analyzed by using two different means of relating the HC emissions and the resulting O_x concentrations.

The first HC/O_x relationship is based on a nonlinear upper limit curve (Schuck and Papetti 1973). The upper limit curve enclosed the highest O_x values observed for a given HC concentration. The relationship is approximated by Equation 1:

$$HC = 2.049\ O_x - 4.792\ O_x^2 + 5.036\ O_x^3 \qquad (1)$$

For a given base year O_x concentration, Equation 1 is used to calculate a corresponding HC concentration (6-99 am). Assuming a proportional relationship between HC emissions and the HC concentration, a new HC concentration is projected for the year of interest. Then, the relationship implied by Equation 1 is used to estimate the O_x concentration corresponding to the new HC concentration for the projection year.

The second HC/O_x relationship assumes that the O_x concentration is a linear function of HC emissions. Therefore, a change in HC emissions is assumed to result in a proportional change in O_x concentrations.

Both of the above calculation procedures assume a zero background concentration of HC and O_x.

ASSUMPTIONS USED IN MODELING

Projections of O_x air quality were made for 37 areas in the United States. The assumptions on which the O_x projections are based are summarized in Table 1.

Four assumptions are made which immediately affect the quantity of estimated HC emissions from mobile sources. First, for light-duty vehicles one of several possible emission standards for HC is assumed to take effect in 1978. Second, the replacement rate for light-duty vehicles is assumed to result in a complete turnover in the vehicle population every 13 years. Next, the deterioration rate of control devices for mobile sources is reduced from the present rate by assuming that inspection and maintenance plans will be in operation. Credits for inspection and maintenance are calculated using the assumptions listed in AP-42, Supplement 5 (EPA 1976). Lastly, the exhaust emissions for light-duty trucks and gasoline and diesel-powered heavy-duty vehicles are projected based on the emission factors of AP-42. It should be noted that the emission reduction assumed for these latter vehicles is generally less than that assumed for light-duty vehicles.

TABLE 1. ASSUMPTIONS FOR HYDROCARBON/OXIDANT AIR QUALITY PROJECTIONS

Emission Source Category	Emission Standards* in Grams Per Mile	Emission Factor Ratio of Emission to Base Year					Compounded Growth Rate
Light Duty Vehicles		1964	1970	1980	1990	2000	
1970 Emissions =	2.0	1.48	1.0	.41	.21	.20	3.0%
10.3 grams/mile	1.5+	1.48	1.0	.40	.17	.17	
Emission Standards	.9	1.48	1.0	.38	.12	.12	
applied to model years	.4++	1.48	1.0	.37	.09	.08	
1978 and beyond	.1	1.48	1.0	.36	.06	.06	
Other Mobile Sources							
Light-Duty Trucks		1.48	1.0	.39	.14	.14	3.0%
Heavy Duty Gasoline		1.11	1.0	.65	.18	.15	
Heavy-Duty Diesel		1.0	1.0	.87	.27	.23	
Stationary Sources		1.0	1.0	.85	.50	.25	3.2%

*Current emission standards apply until above changes occur.

+Present Interim Emission Standard.

++Statutory Emission Standard.

Growth rates have a major effect on HC emissions projected to future years. A growth rate of three percent compounded annually was selected for all mobile sources. This growth rate is representative of the historical growth in vehicle miles traveled in metropolitan areas. Stationary source growth rates were estimated from economic indicators from four groupings of sources: electric generation units, industrial activities, area sources and miscellaneous point sources. The stationary sources of HC are expected to grow at a 3.2 percent compounded rate.

PAST TRENDS

To help assess some of the assumptions used in the projective air quality models a study has been made of past trends in O_x air quality and estimated HC emissions. For this comparison, the most effective sets of data come from California. In general, trends in air quality have followed the trends in HC emissions. For example, in Los Angeles HC emissions have been decreasing steadily since the mid-1960's. It was estimated that the average emissions of HC have decreased by 15 to 18 percent between 1964 and 1974 in Los Angeles; during this same period peak O_x concentrations for six locations in Los Angeles have decreased an average of 20 percent (Trijonis et al. 1976).

Figure 1 presents a summary of the observed changes in O_x concentrations in the Los Angeles Air Quality Control Program (AQCR). In addition, O_x concentration projections are shown. The upper trend line represents the monitoring site with the least improvement in O_x concentration from 1964 to 1974, and the lower line represents the site with the most improvement. The middle trend line is the median of six sites in the AQCR.

Noting that the projection lines are in agreement with the general trend in air quality, it appears that the assumptions concerning the relationships between HC emissions and O_x concentrations are reasonable.

PROJECTION RESULTS

For the areas that were modeled, the base year concentration was the second highest one-hour annual average for 1972-1974. Table 2 shows the results of the upper-limit curve projections for an HC emission standard of 0.4 grams/mile. These calculations showed an average improvement in O_x air quality of 15 percent by 1980, 42 percent by 1990 and 50 percent by 2000. As mentioned previously, these projections depend on the growth assumptions and the assumption concerning implementation of the emission standard in 1978.

In spite of these improvements in O_x air quality many areas are not projected to meet the ambient standard for O_x by 2000. Table 2 shows that 26 of the 37 areas modeled will have concentrations in excess of the 0.08 ppm standard in 2000. In addition, none of these cities is projected to have O_x concentrations which are at least twice the standard.

It should also be noted that there is a significant difference in the results obtained for the two models used. A comparison of the effect for

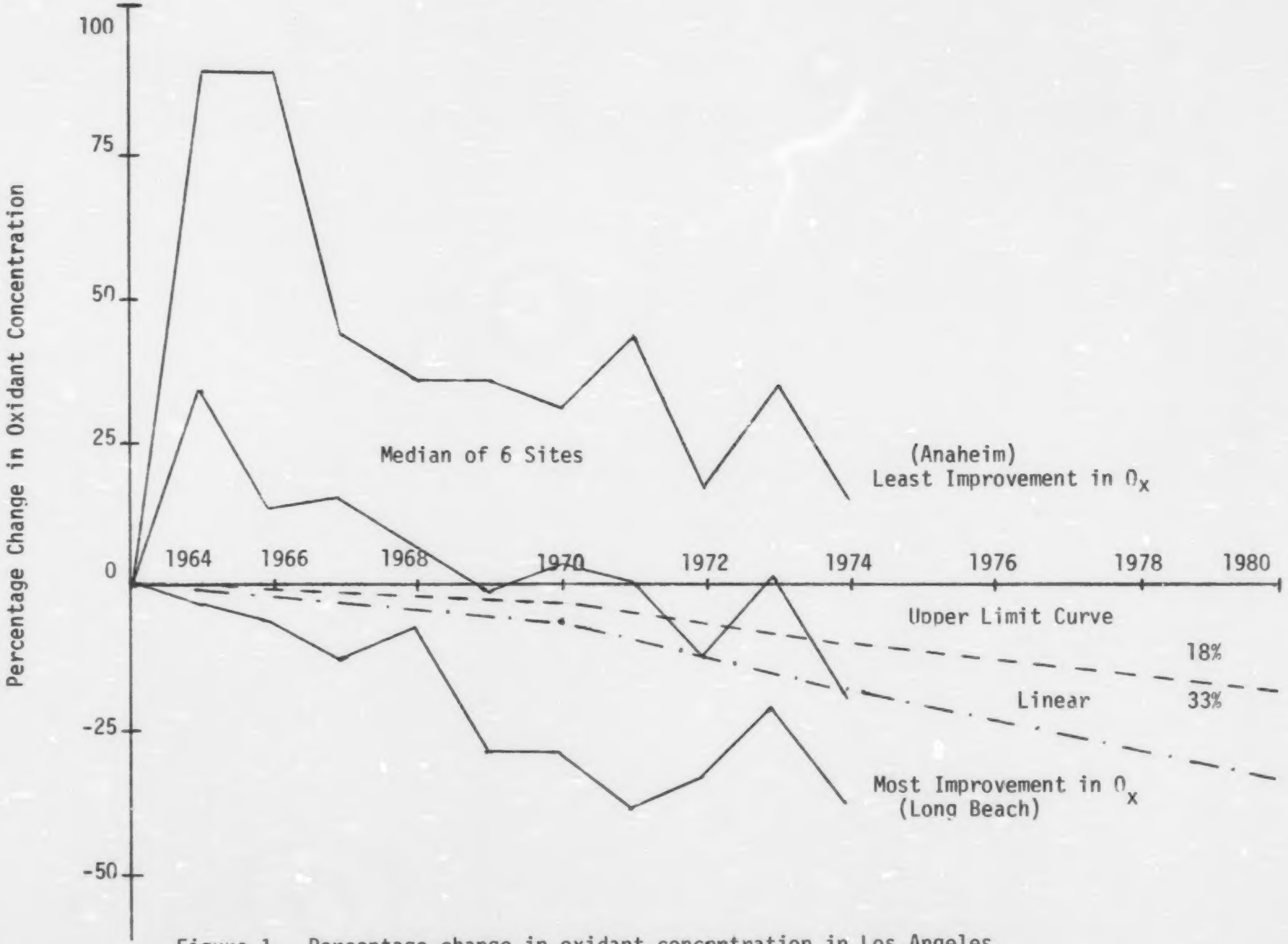

Figure 1. Percentage change in oxidant concentration in Los Angeles AQCR (1964-1980).

TABLE 2. PROJECTED OXIDANT AIR QUALITY*

	BASE YEAR CONCENTRATION (PPM)	1980 CONCENTRATION (PPM)	1990 CONCENTRATION (PPM)	2000 CONCENTRATION (PPM)
004 Birmingham	.29	.24	.17	.15
005 Mob.-Pensacola	.29	.24	.17	.15
013 Clark-Mohave	.22	.18	.12	.10
015 Phoenix-Tucson	.19	.15	.10	.08
024 Los Angeles	.54	.46	.34	.30
028 Sacramento Valley	.28	.25	.18	.15
029 San Diego	.32	.25	.16	.15
030 San Francisco	.33	.29	.22	.18
031 San Joaquin	.27	.24	.18	.15
033 SE Desert	.32	.28	.21	.17
036 Denver	.33	.26	.16	.15
043 NY-NJ-Conn.	.36	.30	.20	.18
045 Philadelphia	.20	.15	.09	.08
047 Nat. Capitol	.38	.30	.19	.18
067 Chicago	.30	.29	.23	.18
070 St. Louis	.39	.36	.28	.23
079 Cincinnati	.19	.15	.10	.09
105 S Lou-SE Texas	.32	.28	.20	.17
115 Baltimore	.23	.22	.17	.14
119 Boston	.21	.17	.11	.10
131 Minn-St. Paul	.10	.08	.05	.04
153 El Paso	.13	.09	.05	.05
160 Gnsse-Fngr Lks.	.12	.09	.05	.04
173 Dayton	.16	.13	.08	.07
193 Portland	.15	.13	.08	.07
197 S.W. Penna.	.17	.14	.09	.08
214 Corpus-Christi	.15	.15	.12	.09
215 Dallas-Ft. Wrth	.19	.16	.10	.09
216 Houston-Glvstn	.38	.36	.29	.24
229 Puget Sound	.13	.09	.05	.05
991 Region 1	.19	.16	.11	.09
992 Region 2	.19	.16	.11	.09
993 Region 3	.19	.19	.15	.12
994 Region 4	.17	.16	.11	.09
995 Region 5	.17	.14	.09	.08
996 Region 6	.20	.19	.15	.12
997 Region 7	.11	.09	.06	.05
Average Percent Decrease		15.	42.	50.
No. Cities Above Std.		36	30	26

*Light Duty Vehicle Emission Standard = 0.4 grams/mile

Projected Conc: Second highest 1-hour concentration in ppm
Base Year: Base Year concentration is second highest 1-hour annual average recorded from 1971 to 1974

various assumptions concerning HC emissions and O_x background concentrations on the long-range projections to the year 2000 is presented in Table 3. At the statutory emission standard of 0.4 grams/mile the empirical upper-limit relation projects an average air quality improvement of 50 percent by the year 2000. The linear assumption projects an average improvement of 61 percent if background O_x concentrations are neglected and a 46 percent improvement if a 0.05 ppm background is assumed.

These differences represent the average improvement for 37 areas. Individual cities may show improvements that differ from these average changes because of the different magnitudes of base-year concentrations. For example, a background concentration will have a smaller effect on the projected improvement in cities with high O_x concentrations than for cities with low concentrations. In addition, there will be less difference between the results of the two projective models for cities with low concentrations than for cities with high concentrations. These effects are illustrated by comparing the number of cities which are projected to violate the ambient air quality standard in 2000. With an emission standard of 0.4 grams/mile the upper-limit curve projects that 70 percent of the cities considered will still be in violation of the air quality standard in 2000. The linear assumption with zero background projects that this number will be reduced to 49 percent. However, when the background of 0.05 ppm is used, the number of cities in violation of the standard is projected to be 86 percent.

SUMMARY

The methods used to predict O_x concentrations indicate that even under stringent control measures the O_x standard will not be met in many cities. It is predicted, however, that the O_x concentrations can be reduced by as much as 46 to 61 percent under the most optimistic assumptions.

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TABLE 3. AIR QUALITY PROJECTIONS FOR PHOTOCHEMICAL OXIDANTS

	Cases							
Assumptions	1	2	3	4	5*	6	7	8
Light Duty Vehicle Standard - g/mile	.4	1.5	.4	.9	.4	.1	.4	.4
Light Duty Vehicle Growth Rate - %	3	3	3	3	3	3	1	3
Stationary Source Control - %	50	75	75	75	75	75	75	75
Oxidant Projection Method	UL+	UL+	L_1++	UL+	UL+	UL+	UL+	L_2+++
Average Percentage Improvement from 1970 to 2000**	29	41	46	46	50	52	54	61
Percent of Areas Above .08 ppm in 2000**	86	84	86	76	70	62	59	49

*Most Reasonable Estimate

**Based on 30 Urban Areas and 7 Larger Regions

+UL = Upper Limit Curve

++L_1 = Linear with .05 ppm background conc.

+++L_2 = Linear with zero background

TRENDS IN AMBIENT LEVELS OF OXIDANT AND THEIR POSSIBLE UNDERLYING EXPLANATIONS

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ABSTRACT

This paper describes work underway within the Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, to review and evaluate trends of ambient oxidant/ozone concentrations at sites in the nation that have suitable amounts of historical data. Among the trend parameters being examined annually are: (1) the second highest hourly concentration; (2) the average daily maximum hourly concentration; and (3) the percent of days with valid hourly readings exceeding the National Ambient Air Quality Standard. In areas having more than one site, special emphasis is given to the spatial variation of trends.

Trends in oxidant/ozone levels are also being examined in relation to hydrocarbon and nitrogen oxides emission trends. A major objective of evaluating these relationships is to determine if trend analysis can be used to evaluate the effectiveness of oxidant control programs. Ambient oxidant/ozone trends and corresponding emission trend data have been examined in several California Air Basins; Denver, Colorado; Philadelphia, Pennsylvania; and a non-urban site in western Maryland.

In areas where statistically significant trends in ambient oxidant/ozone levels have been found, there was reasonable correspondence to trends in hydrocarbon emissions. However, the combined hydrocarbon and oxides of nitrogen emission trends were found to be more significantly correlated to oxidant/ozone trends than those of hydrocarbon emissions alone.

INTRODUCTION AND BACKGROUND

In several locations across the United States, where attainment of the National Ambient Air Quality Standards (NAAQS) for photochemical oxidants (O_x) (0.08 ppm — one hour average) is unlikely, additional measures to reduce

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precursor emissions are necessary. Since these measures may sometimes be expensive or difficult to implement, the question arises, "Have past emission controls been effective in improving ambient concentrations of photochemical O_x or ozone (O_3)"? Perhaps an effective means for answering such a question is through ambient air quality trend analysis.

Observed ambient O_x/O_3 trends are likely to depend upon a number of factors. Among these factors are population and industrial growth patterns, trends in non-methane hydrocarbons (NMHC) emissions, changes in reactivity of the organic mix, trends in emissions or ambient concentrations of oxides of nitrogen (NO_x) and annual variations in the frequency of meteorological conditions conducive to photochemical O_x formation. It should be noted that in the U.S., O_x/O_3 control strategies have stressed reductions in non-methane or reactive NMHC or RHC emissions.

Results of O_x/O_3 trend studies have been reported in the literature. Notable among these have been those of Altshuller (1) and Trijonis et al. (2).

Altshuller (1) reviewed data from six Continuous Air Monitoring Program (CAMP) sites in the United States. These were central city sites located in the following U. S. cities: Chicago, Cincinnati, Denver, Philadelphia, St. Louis, and Washington, D. C. He noted significant reductions both in observed levels of ambient O_x/O_3 and in the frequency of high levels between the two periods studied, 1964-66 and 1971-73, at five of the six sites. The reductions in the frequency of the highest concentrations (>0.125 ppm) appeared to be the most dramatic, ranging from 67 to 94 percent at the stations exhibiting downward trends. Perhaps a portion of these long-term trends could have resulted from downward trends in NMHC emissions and upward trends in local nitric oxide (NO) emissions from motor vehicles between the two periods. However, no concerted effort was made to relate ambient O_x trends to precursor emission trends.

A comprehensive analysis of air quality and the relation to emission trends in the California South Coast Air Basin (i.e., Los Angeles area) was prepared by Trijonis et al. (2) in a California Institute of Technology report. Table 1 provides a synopsis of emission and air quality trends presented in the Cal. Tech. report. The analysis covered the 10-year period 1965-74. An approximation of the prevailing wind direction can be thought of as oriented from west to east or left to right in the table. In general, the large geographical differences in HC and NO_x emission trends were found to agree reasonably well with the observed geographical variations in ambient O_x (average daily 1-hour maximum) and NO_2 (annual average) concentration trends. In evaluating geographical agreement between ambient O_x and precursor emission trends, consideration of local NO depletion and transport must be taken into account. Overall, the Basin-wide trends indicated:

(1) a 36 percent increase in NO_x emissions was accompanied by a 35 percent increase in nitrogen dioxide (NO_2) concentrations; and

(2) an 18 percent reduction in reactive HC emissions was accompanied by a 19 percent reduction in ambient levels of O_x. The Cal. Tech. analysis provides strong evidence that reduction of organic pollutants reduces

TABLE 1. EMISSIONS AND AIR QUALITY TRENDS IN THE SOUTH COAST AIR BASIN, 1965-1974

	PREVAILING WIND DIRECTION →						BASIN-WIDE AVERAGE
COUNTY	SANTA BARBARA	VENTURA	LOS ANGELES	ORANGE	RIVERSIDE	SAN BERNARDINO	
% CHANGE IN RHC EMISSIONS	− 9%	− 2%	−24%	+ 6%	− 8%	− 17%	−18%
% CHANGE IN NO_x EMISSIONS	+69%	+42%	+25%	+89%	+69%	+38%	+36%
% CHANGE IN COUNTY-WIDE OXIDANT (# OF STATIONS)	NO DATA	NO DATA	− 31% (8 SITES)	− 12%* (2 SITES)	+12% (2 SITES)	+ 2% (1 SITE)	− 19% (13 SITES)
% CHANGE IN COUNTY-WIDE NO_2 (# OF STATIONS)	NO DATA	NO DATA	+19% (8 SITES)	+93% (2 SITES)	NO DATA	+47% (1 SITE)	+35% (11 SITES)
% OF BASIN POPULATION (1970)	2.6	3.7	68.7	13.9	4.5	6.7	

*ONE SITE REPORTED AN INCREASE OF +78%, THE OTHER A DECREASE OF -31%

(FROM TRIJONIS ET AL. - REF 2)

ambient levels of O_x. However, an increase in NO_x emissions especially in the vicinity of the O_x monitoring sites may have influenced the ambient O_x reductions.

More recently, Pacific Environmental Services, Inc. (PES), in a study done for the U. S. Environmental Protection Agency (EPA), performed an analysis of trends in ambient O_x/O_3 and precursor emission levels for areas where these trends have not previously been extensively evaluated. The remainder of this paper describes the PES Study and its principal findings (3) supplemented by related trend analyses performed within EPA.

DESCRIPTION OF TRENDS DATA

In the PES Study, consideration was limited to locations other than the Los Angeles Basin with 5 or more consecutive years of rather complete data. At least a 5-year period was considered to be necessary to minimize possible meteorological biases. If the period of record is much shorter, the meteorological influences on air quality trends are likely to be dominant. Over a sufficiently long period, variations due to meteorological anomalies are likely to be identified and the effects of emission changes, growth, etc. probably will have a more consistent influence on ambient trends.

Initially, only the years 1970-74 were considered. This period had the broadest common data base. Yet nearly all the suitable ambient data sites were located in California. Changes in analytical method, missing data, changes in monitoring locations or, as was often the case, a brief history of monitoring for O_x/O_3 limited the base of suitable trends data outside of California. Suitable sites were located in the San Francisco Bay Area (9 sites), San Joaquin Air Basin (Stockton, Modesto), Southeast Desert Air Basin (Lancaster), Sacramento Valley Air Basin (Redding), North Central Coast Air Basin (Salinas), all in California; and in Denver, Colorado; and Philadelphia, Pennsylvania. In addition to the ambient data, HC and NO_x emissions data for the individual years 1970 through 1974 or information that would have indicated the relative trend during the period were obtained, as available, from EPA and state/local air pollution control agencies.

Ambient trend data were also examined for a non-urban site, Garrett County, Maryland, located in the extreme western part of the state. This non-urban site was the only one found to have a rather lengthy period of record (4 years). However, measurements were taken only during the summer O_x season. For this particular site, only ambient data and apparent trends, if any, were to be noted. No attempt was to be made to evaluate the relation to emission trends since there is presently no reasonable, non-arbitrary means of assigning an area of emissions that would significantly affect a remote non-urban site.

A map of the California Air Basins and station locations outside the Bay Area Air Basin are shown in Figure 1. Figure 2 shows station locations in the Bay Area Air Basin. Site locations outside of California are shown in Figure 3.

DATA ANALYSIS AND INTERPRETATION

The following ambient O_x/O_3 trend parameters were analyzed at each urban site annually, the:

- 2nd high hourly concentration
- annual average daily maximum hourly concentration
- third quarter average daily maximum hourly concentration
- frequency of days with hourly concentrations greater than 0.08 ppm (NAAQS)
- frequency of days with hourly concentrations greater than 0.16 ppm (2 x NAAQS).

Table 2 shows the indicated direction of the first four trend parameters at all sites during 1970-74. The fifth parameter, values greater than 0.16 ppm, occurred too infrequently to evaluate trends. Note that different trend parameters may indicate contrasting trend directions. Only the trends of the pooled values of the 2nd high concentration in the San Francisco Bay Area and the average daily maximum in Denver proved to be statistically significant at the 5 percent level. The trends were downward in both cases.

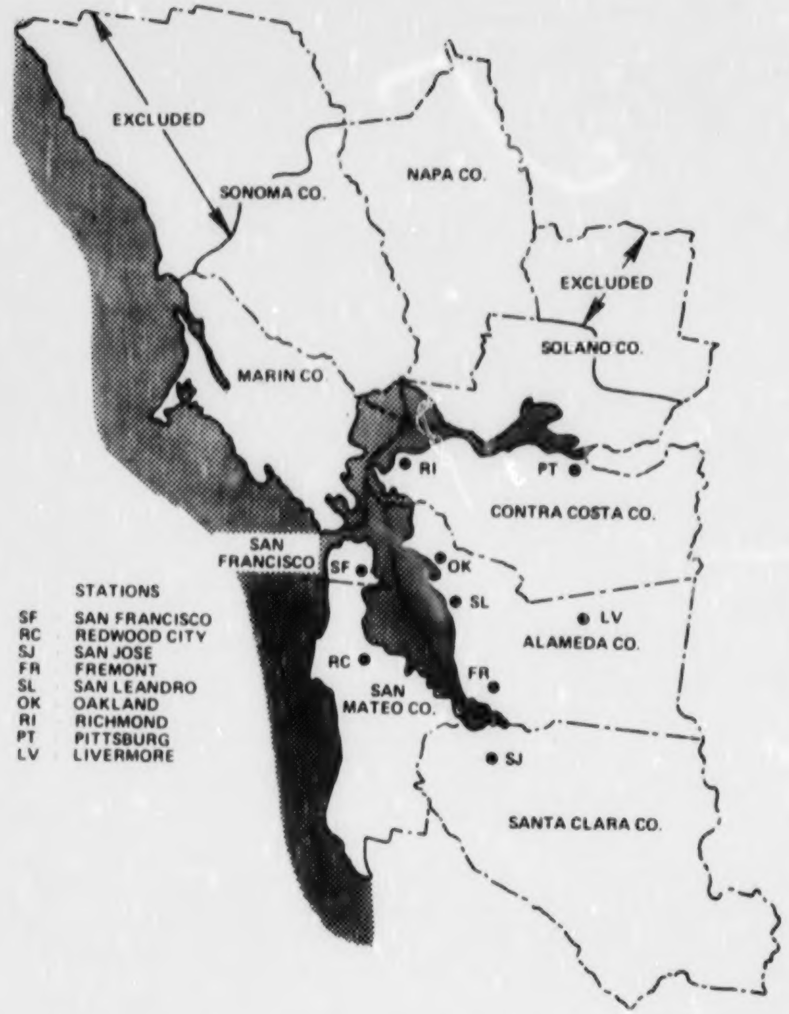

Figure 1. Bay area air basin station locations.

TABLE 2. TREND DIRECTIONS FOR VARIOUS OXIDANT INDICES, AT INDICATED MONITORING STATIONS, 1970-74

	SF	RC	SJ	FR	SL	OK	RI	PT	LV	RD	ST	MO	SA	LN	DV	PH
SECOND-HIGH	–	–	+	–	–	–	–	–	–	0	+	–	+	+	–	+
AVERAGE MAX.	–	+	+	+	+	+	–	–	+	+	+	–	+	+	–	+
3RD QTR. AVG. MAX.	–	–	+	–	+	–	–	–	+	+	+	–	+	+	–	+
FREQUENCY > 0.08 ppm	–	–	+	–	–	–	–	–	+	+	+	–	+	+	+	–

STATIONS

SF - SAN FRANCISCO
RC - REDWOOD CITY
SJ - SAN JOSE
FR - FREMONT
SL - SAN LEANDRO
OK - OAKLAND
RI - RICHMOND
PT - PITTSBURG
LV - LIVERMORE
RD - REDDING
ST - STOCKTON
MO - MODESTO
SA - SALINAS
LN - LANCASTER
DV - DENVER
PH - PHILADELPHIA

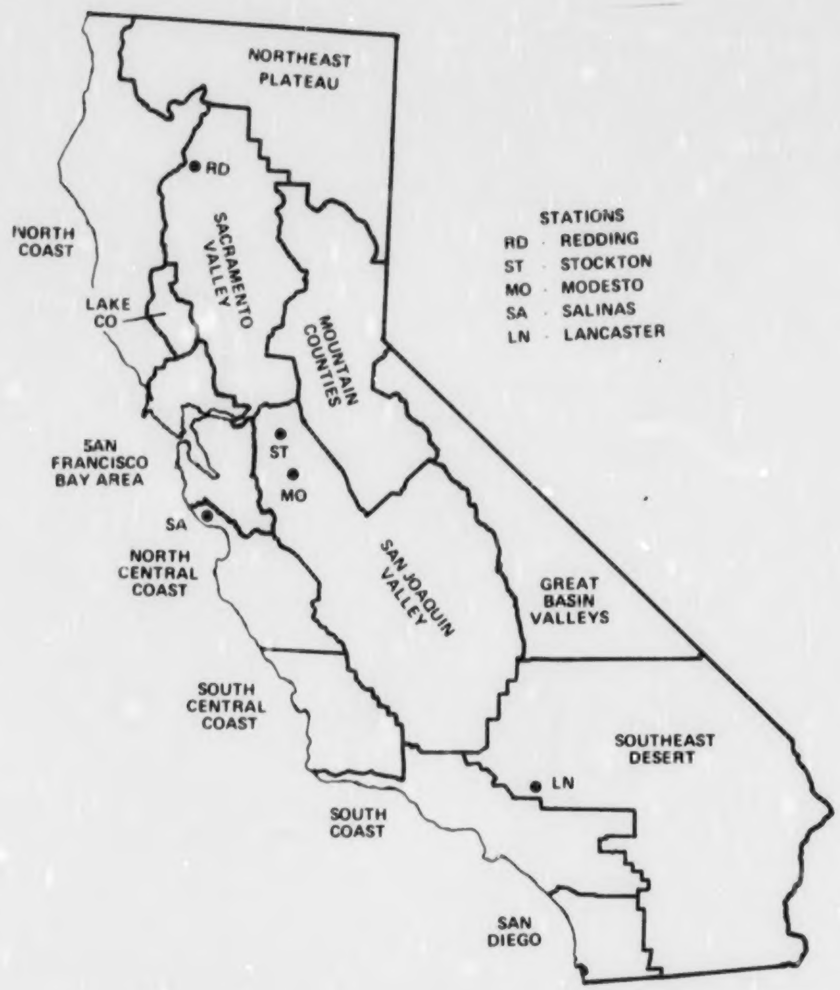

Figure 2. California air basin station locations (Outside San Francisco Bay area).

Since the emission data from the Denver vicinity were not available in sufficiently detailed form, evaluation of relation between ambient data and emissions could not be made. Therefore, the San Francisco Bay Area was the only area (outside of Los Angeles) with sufficient information to analyze for the relation of HC and NO_x emission trends or control programs to definitive O_x trends.

The ambient O_x data showing significant trends in the Bay Area are shown in Table 3. Note the large improvement in western areas of the Basin in contrast to eastern areas (e.g. San Jose and Livermore). Table 4 is indicative of HC and NO_x emissions trends in the Bay Area during the 1970-74 period (in box). Table 4 shows that overall emissions have not changed much in the most recent five years. Only HC emissions show a slight but gradual decrease.

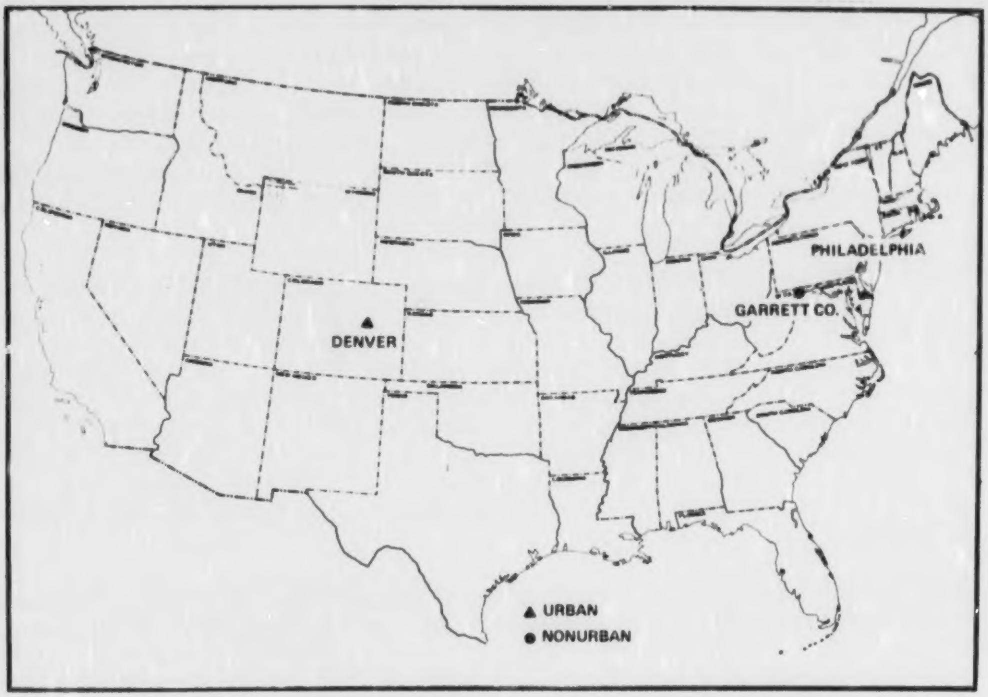

Figure 3. Station locations outside California.

TABLE 3. OXIDANT LEVEL BY YEAR AND TREND DIRECTION (2ND HIGHEST DAILY MAX. HOURLY AVG., PPM)

	'70	'71	'72	'73	'74	TREND
SAN FRANCISCO (SF)	.14	.15	.07	.08	.06	–
REDWOOD CITY (RC)	.16	.16	.17	.12	.16	–
SAN JOSE (SJ)	.16	.14	.17	.18	.26	+
FREMONT (FR)	.27	.24	.29	.18	.21	–
SAN LEANDRO (SL)	.21	.24	.14	.20	.17	–
OAKLAND (OK)	.20	.21	.09	.14	.09	–
RICHMOND (RI)	.18	.14	.10	.10	.08	–
PITTSBURG (PT)	.18	.18	.18	.10	.10	–
LIVERMORE (LV)	.29	.21	.18	.20	25	–

TABLE 4. ESTIMATED EMISSIONS* AND COMBINED EMISSION RATIOS FOR HYDROCARBON AND OXIDES OF NITROGEN IN SAN FRANCISCO BAY AREA, 1962 - 1974

YEAR	HC	NO_x	HC/NO_x
1962	1300	490	2.65
1963	1300	500	2.60
1964	1400	550	2.55
1965	1300	550	2.36
1966	1300	620	2.10
1967	1300	620	2.10
1968	1300	670	1.94
1969	1300	700	1.86
1970	1140	740	1.54
1971	1110	740	1.50
1972	1130	790	1.43
1973	1070	820	1.30
1974	1030	720	1.43

*TONS PER DAY

However, more detailed emissions data by county (not shown) and source type (stationary or mobile) indicate that: (1) significant HC emission reductions have been achieved in the western part of the Bay Area; and, (2) mobile sources NO_x emissions have increased in most places. Air quality and emissions trends reflect new auto and stationary source emission control programs and differential area growth patterns. Notably, some eastern areas of the Basin have undergone rapid growth, thus overshadowing beneficial effects of emission control programs.

The correlation coefficient between pooled second highest O_x concentrations in the Bay Area and regionwide HC emissions was only + 0.58, not statistically greater than zero at the 5 percent level. The significance test involves the Student t test, as explained by Moroney (4). The correlation was greater when both HC and NO_x emission trends were related to oxidant trends. The relation between HC/NO_x emission ratio and second highest O_x levels was considerably higher at + 0.88 and statistically significant at the 5 percent level. The improved results are indicative of the important role of NO_x in the photochemical process. In these results the variable effect of meteorological factors was not considered.

A much clearer picture for the Bay Area emerges when 13 years of data are examined and normalized by considering only days with photochemical O_x conducive meteorological conditions. Table 5 denotes the normalized O_x trends. Over the 13-year period for which data are available, the downward trend was found to be highly significant ($p<.001$). Thus, it is virtually certain (i.e. 99.9 percent) that improvement in the Bay Area oxidant levels is attributable to some physical phenomena rather than chance. The possibility that the improvement was unduly influenced by meteorological factors was minimized by the long period of record and consideration of ambient O_x levels only for days with similar meteorological conditions. Table 4 shows basin-wide HC and NO_x emission trends for 1962-74. Note the much wider range of emissions occurring during this longer period. When HC emissions (see Table 4) were correlated with normalized O_x levels pooled for the six stations having complete records over the 13-year period (1962-74), a correlation coefficient of + 0.77, statistically significant at the 5 percent level, was found. Moreover, the correlation coefficient between O_x and HC/NO_x emission ratio trends was even more highly significant, + 0.92, significant at the 0.1 percent level.

The available O_3 trend parameter data for the non-urban station at Garrett County, Maryland, is given in Table 6. No apparent trends were noted. What seems evident, however, are considerably large fluctuations in some of the statistics from year to year. For instance, the percent of hours that the hourly concentration exceeded the ambient standard varied by more than a factor of 3. Probably, these variations in the large-scale regional O_x/O_3 levels may be reflected in the levels experienced in urban areas.

An obvious deficiency of this paper was the lack of suitable trends information outside of California. Improvement in the trend data base, however, is forthcoming. At least ten states outside of California now have sites with three consecutive years of O_x/O_3 measurements. These data will eventually provide a data base for assessing nationwide O_x trends and their probable causes.

TABLE 5. AVERAGE HIGH-HOUR OXIDANT CONCENTRATIONS FOR DAYS WITH COMPARABLE TEMPERATURE AND INVERSION CONDITIONS (APRIL THROUGH OCTOBER OXIDANT SMOG SEASONS, 1962 - 1974)

	AVERAGE HIGH-HOUR OXIDANT CONCENTRATION (IN PARTS PER MILLION)														OXIDANT TREND DIRECTION	
MONITORING STATIONS	'62	'63	'64	'65	'66	'67	'68	'69	'70	'71	'72	'73	'74	13 YEAR	1970 - 74 ONLY	ALL DATA
SAN FRANCISCO (SF)	.14	.12	.15	.09	.08	.08	.05	.04	.07	.05	.03	.04	.06	.08	–	–
SAN LEANDRO (SL)	.13	.16	.19	.10	.14	.12	.11	.12	.12	.11	.10	.11	.10	.13	–	–
SAN JOSE (SJ)	.11	.17	.14	.16	.11	.13	.13	.13	.12	.08	.10	.11	.16	.13	+	–
REDWOOD CITY (RC)	.13	.10	.10	.14	.10	.09	.06	.09	.08	.07	.08	.07	.07	.09	–	–
WALNUT CREEK (WC)	.10	.11	.10	.11	.10	.13	.10	.13	.09	.09	.09	.08	.08	.10	–	–
SAN RAFAEL (SR)	.08	.09	.07	.08	.07	.07	.06	.07	.08	.07	.05	.05	.06	.07	–	–
BAAPCD AVERAGE*	.12	.12	.13	.13	.10	.10	.09	.10	.09	.08	.08	.08	.09	.10	–	–
LIVERMORE**	--	--	--	--	--	.13	.18	.18	.13	.11	.09	.12	.13	.13	+	–

*FOR BENCHMARK STATIONS ABOVE, WITH 13 YEARS OF RECORD

**STATION WITH 8 YEARS OF RECORD

-- NO DATA

(SOURCE: INFORMATION BULLETIN 3-25-75: A STUDY OF OXIDANT CONCENTRATION TRENDS: TECHNICAL SERVICES DIVISION, BAY AREA AIR POLLUTION CONTROL DISTRICT)

TABLE 6. OXIDANT/OZONE TREND STATISTICS FOR GARRETT CO., MARYLAND

STATISTIC	YEAR				
	'70	'71*	'72	'73	'74
MAX HOURLY CONC. (ppm)	0.13	--	0.12	0.15	0.15
MEAN HOURLY CONC. (ppm)	0.05	--	0.05	0.07	0.06
% DAYS HOURLY CONC. > 0.08 ppm	40	--	40	78	43
% HOURS CONC. > 0.08 ppm	27	--	11	37	13

*NO SAMPLING PERFORMED IN 1971

REVIEW AND CONCLUSIONS

The following statements summarize trends information as described in this report. Long-term trends in oxidant in the Bay Area Air Basin are significantly related to trends in HC emissions. Oxidant concentrations in the Bay Area are more highly related to HC/NO_x emission ratios. This indicates reductions in NO_x emissions may have a tendency to increase O_x levels within the Basin. Oxidant problems in the Bay Area, due to changing patterns of precursor emissions, are becoming more severe in inland locations than in Bayside locations. Monitoring data for a 5-year period may not, in general be sufficient to establish statistically significant O_x trends in an area. And concentrations of O_x/O_3 in non-urban locations exhibit large fluctuations from year to year that may have an influence on urban oxidant levels.

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SESSION 23

ON THE OZONE/OXIDANT CONTROL STRATEGY IN U.S.

Chairman: A.B. Bromley
OECD, France

TRENDS IN PHOTOCHEMICAL OXIDANT CONTROL STRATEGY

J. Padgett*

ABSTRACT

The national ambient air quality standard for oxidants was promulgated by the U. S. Environmental Protection Agency in April, 1971. Critical reviews of the scientific evidence of health and other adverse effects support this standard although data limitations even today provide ample opportunity to challenge it. The basic Environmental Protection Agency strategy for the control of oxidant is to control anthropogenic emissions of organic compounds that can react photochemically to form oxidants. It seems clear that this approach is sound even though much additional research is needed to answer questions associated with the effects of oxidants and the best approach to their control. Oxidants originally were of concern only in large cities, but recent technical findings show that high oxidant levels (exceeding the standard) can occur over large geographical areas because of the transport of oxidants and their precursors over a several day period. Given enough time, even low reactive organics can form oxidants and are of concern. The emerging oxidant control strategy therefore places more emphasis on the control of all organics emitted within large geographical areas. In parallel with the continuing implementation of oxidant control plans in many urban areas, the Environmental Protection Agency is developing new source regulations to control organic emissions from chemical plants. Guidelines and regulations are also being developed to effectively reduce organic emissions from other new and existing sources, and States are encouraged to apply reasonably available emission controls over broad geographical areas where emission densities are relatively high.

INTRODUCTION

To protect the public from the harmful effects of photochemical oxidant, the U.S. Environmental Protection Agency (EPA) promulgated a national ambient air quality standard in April, 1971(1). This standard placed a limit on the amount of photochemical oxidant that could be present in the air after July, 1975 (with some provisions for extending this deadline for two years), based on the best available scientific evidence of health and other adverse effects(2). Many difficulties have been encountered as federal, state, and local governments have attempted to implement air pollution control programs which would ensure that the standard would be met. Even today, there are many places in the country that experience photochemical oxidant levels substantially in excess of the standard.

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Our basic oxidant control strategy is to reduce anthropogenic emissions of organic compounds that can react photochemically to form oxidants. Even though the rationale for this approach is well documented(3), questions still are raised by community and industry leaders responsible for implementing it. Typical questions are: Why do we need to meet the oxidant standard? Are we concerned only with ozone (which is the pollutant we monitor) or with all oxidants? Is the basic strategy of reducing hydrocarbons a valid one? What is the impact on control strategies of hydrocarbon reactivity, background oxidant levels, and the transport of oxidants and their precursor into and out of a community?

There are as yet no simple non-controversial answers to many of the above questions. And in some cases, as you have heard at this conference, scientific opinion is sharply divided on the answers to these and other questions we could ask. But if we are to succeed in our national goal of oxidant control, it is important for the public, as well as the scientific community, to have answers to these questions and to be convinced that the control strategies we employ are needed and will be effective. Conferences such as this are a vital part of this process. Also important is the support of independent scientific organizations such as the National Academy of Sciences, which stated in its comprehensive 1976 report on Ozone and Other Photochemical Oxidants(4) the following:

> Despite uncertainties concerning the causative agents and their effects, we must proceed with the regulation of emissions that lead to the formation of photochemical smog. At the same time, research should continue on identifying the individual harmful agents in photochemical smog and their effects.

This paper first will consider briefly the scientific support for the oxidant standard. We then will describe the current EPA control strategy for oxidant control and how this strategy is evolving as a result of new research findings. We will not, however, attempt in this brief paper to try to answer all of the questions we have posed.

SUPPORT FOR THE OXIDANT STANDARD

The U. S. national ambient air quality standard for photochemical oxidants is 0.08 parts per million (ppm). This is an hourly average, not to be exceeded more than once per year. While few will disagree that high concentration levels of ozone and other oxidant cause serious adverse health effects, some people question the need for such a restrictive standard, and others question the basis on which the current standard was established. A summary of the health implications of oxidants is given in Reference 5. Questions continue to arise because the data on human health effects from exposure to low levels of photochemical oxidant still are limited and hence may never be completely settled even though many independent scientific reviews by medical experts support the present standard.

One such study was commissioned in 1974 when Congress asked the National Academy of Sciences (NAS) to review and update the information on health effects from air pollution, including those effects caused by photochemical oxidant. After reviewing and interpreting the available data, these highly qualified scientists from the various scientific and technical fields concluded:

> In general, the evidence that has been accumulated since the promulgation of the Federal ambient air quality standards by the EPA Administrator on April 30, 1971, supports those standards. Hence on the balance, the (NAS) panels found no substantial basis for changing the standards(6).

Although this conclusion applied to all national standards, the NAS, in specifically addressing photochemical oxidant, noted that even with the current standard, the risk to the general population may not be negligible, and that there is evidence which suggests that there may not be a completely safe level of this air pollutant for all people. A similar conclusion has more recently been reached in a report by the World Health Organization (WHO), which states:

> It is apparent that any primary protection standard (for oxidant) between .05 and .10 ppm will provide the narrowest margin of safety against some possible detrimental effects in the more susceptible segments of the population. There would seem to be little justification for exceeding .10 ppm for a primary protection standard(7).

OXIDANT CONTROL STRATEGY

Our understanding of the photochemical oxidant formation process has grown over the years because of both improvements in the theory of photochemical oxidant formation and continuing empirical research. However, from a regulatory point of view, the most significant fact remains that oxidants are formed from two types of precursors: nitrogen oxides and organic compounds (of which hydrocarbons are a major component). In most urban areas, the ratio of the organic concentrations to the concentration of nitrogen oxides is such that the nitrogen oxides are in surplus and hence the organics are the limiting factor in the set of reactions which produce oxidants. Therefore, hydrocarbon and other reactive organic emissions must be reduced in order to lower oxidant levels.

The reductions in emissions of hydrocarbons and other organic compounds are to be achieved through Federal and State programs that have been formalized in regulations promulgated under the Federal Clean Air Act of 1970(8). The Federal programs provide for the reduction in emissions nationwide through the Federal Motor Vehicle Control Program, the Federal program for control of aircraft emissions, and the development of New Source Performance Standards. The State programs provide for additional control measures through State Implementation Plans in those areas of the country where the Federal programs will not be sufficient to meet the air quality standard for oxidants.

Because roughly half of the hydrocarbons emitted to the ambient air in the United States currently is attributable to motor vehicles, a large portion of hydrocarbon reduction is to be achieved through the Federal Motor Vehicle Control Program. This program has required progressively stricter hydrocarbon controls on all light-duty motor vehicles since the 1968 model year. In 1970, the Clean Air Act required that hydrocarbon emissions from light-duty vehicles and engines be reduced by at least 90% from emissions permissible in 1970 model year vehicles. This will eventually require emissions to be reduced to 0.41 grams per mile. Interim standards of 1.5 grams per mile (g/m) are now required on 1975 through 1977 model year vehicles. Regulations also exist to limit hydrocarbon emissions from other types of vehicles such as motorcycles, trucks, buses, and aircraft.

The Clean Air Act also authorizes EPA to promulgate "Standards of Performance for New Stationary Sources". These are standards for new sources which reflect the best demonstrated system of emission control, taking the cost of emission reduction into account. New sources are sources that are constructed or modified after the standard has been proposed.

When Federal programs are not sufficient to meet the oxidant standard, the State is required to develop plans for additional reduction in emission of organic compounds in those areas that will not meet the oxidant standard. The State Implementation Plans include regulations for existing stationary sources as well as the implementation, where necessary, of Transportation Control Plans.

For the development of Implementation Plans, it is necessary to determine how much the emissions of hydrocarbons and other organics must be reduced. It was realized that the relatively simple methods used for directly emitted pollutants were not appropriate for the complex oxidant formation processes. Therefore, an attempt was made to quantify the amount of hydrocarbon reduction required to meet the oxidant standard. In 1970, the data to relate non-methane hydrocarbon to oxidant concentrations were available only from Denver, Los Angeles, Philadelphia, and Washington, D.C. The 6 to 9 a.m. average non-methane hydrocarbon concentrations were plotted against the peak hourly oxidant concentrations observed later in the day at the same measurement sites. The points scattered because of the variations in the conditions that affect oxidant formation. A curved line was drawn to enclose the data points within an upper boundary. This upper limit curve depicted the highest oxidant levels observed for a given hydrocarbon concentration. From this curve the minimum hydrocarbon reductions required to meet the oxidant standard could be calculated. EPA published the result of this calculation as Appendix J in the August 14, 1971 Federal Register. Given a measured maximum oxidant level in an urban area, Appendix J is to be used to determine the amount of hydrocarbon control required in that area. In some cities the measured oxidant levels were above (greater than 0.28 ppm) the applicable range of Appendix J. These cities were permitted to reduce hydrocarbon emissions proportional to the amount that oxidant levels exceeded the standard.

The August 14, 1971 Federal Register also gives emission reductions that are attainable through the application of reasonably available emission control technology. These emission limitations emphasize reduction of total organic compound emissions, rather than substitution of less reactive organic compounds, because of the evidence that few organic compounds are photochemically unreactive. For organic solvent usage, however, such as in surface coatings and dry cleaning, the guidelines present a list of low reactivity compounds that may be considered for exemption for control.

Transportation Control Plans provide for reductions in hydrocarbon emissions beyond the reductions achieved by the Federal Motor Vehicle Control Program and stationary source regulations set forth in approved State Implementation Plans. Transportation Control Plans typically include measures to decrease automobile travel, require inspection and maintenance of vehicles, and limit vapor emissions during gasoline transfer.

RECENT FINDINGS

Recent field investigations and laboratory studies of oxidant formation and control have provided several new insights. It is now apparent that oxidants are a rural as well as an urban problem. Oxidants can be formed over long time periods during stagnant conditions in high pressure systems or during transport of oxidants and precursors. This implies that the long-term behavior of oxidants and precursors is an important contributor to oxidant concentrations. It also implies that less reactive organic compounds, as well as the more reactive compounds, can contribute to observed oxidant levels. There are also natural sources of oxidants which at times may contribute to oxidant concentrations reaching levels near the oxidant standard. The studies indicate, however, that man-made emissions of hydrocarbons are the predominant source of the highest levels of oxidant.

Non-methane hydrocarbon (NMHC) and nitrogen oxides (NO_x) measurements made in relatively remote, sparsely populated areas of the nation show extremely low NO_x levels and NMHC/NO_x ratios that are sufficiently high that control of NMHC may be of little benefit in these areas. For urban areas, however, these ratios appear to be in the range where a hydrocarbon control strategy is effective.

Although the theory of a hydrocarbon control strategy is well established and has been validated in smog chamber tests, only confirmation in an urban environment, which requires years of data because of the predominant year-to-year influence of meteorological conditions, will be convincing to many. Emissions and air quality data are becoming available over a sufficient number of years for a few locations--notably Los Angeles and San Francisco--to allow meaningful statistical analyses of the effectiveness of hydrocarbon emission reductions in reducing oxidant levels. Separate analyses recently completed for these cities do show good correlations between reductions in hydrocarbon emissions and ambient oxidant concentrations.

IMPLICATIONS FOR OXIDANT CONTROL

Based on findings to date. implications for oxidant control include the following:

1. Recent findings support the basic EPA strategy, which emphasizes the reduction of organic emissions in urban areas. In many urban areas, the required reduction in emissions is far greater than can be achieved by use of all reasonably available control technology and it is likely that some cities will not achieve the oxidant standard for many years. This problem has been recognized by Congress as well as the EPA, and legislative amendments have been proposed that grant extensions in time to meet the standard if the city has itself committed to employ all reasonably available control measures to reduce emissions.

2. EPA policy has strongly encouraged the positive reduction of non-methane organics but still recognizes as a useful interim control measure the substitution of low reactivity for high reactivity solvents. Since even a low reactivity organic may contribute in time to oxidant formation, the use of solvent substitution, even as an interim measure, is now being reexamined.

There is growing recognition that organic emission controls often should extend far beyond the boundaries of a defined urban area. Statewide or even multi-state control of organic emissions may be effective in reducing oxidants in populated regions such as the northeastern United States. At the same time, however, emission control in remote rural regions of the nation, such as portions of the northwestern United States, where NO_x emissions are very low, may be counter-productive. Further study and analysis is needed to better define this problem.

4. Our improved understanding of the mechanisms for formation of oxidant and the role of transport emphasizes the long existing need for improved predictive models to replace the present Appendix J curve that relates peak oxidant concentrations to non-methane hydrocarbon emissions. The use of improved models will not necessarily affect our current control programs, particularly in urban areas where required emission reductions are far greater than can be achieved, but they will establish more accurately long-range program goals and facilitate the development of more effective area wide control programs.

ACTIVITIES IN SUPPORT OF EPA's OXIDANT CONTROL STRATEGY

In addition to the extensive research programs needed to provide better answers to basic questions such as those posed earlier in this paper, a number of other activities associated with control implementation are underway. These include:

1. Model Regulations to limit organic emissions from existing plants, based on reasonably available control technology, are being completed for the paint and coating industries. New regulations for inspection and maintenance programs and the recovery of emissions during gasoline transfer also are in preparation. These will provide guidance to states which may incorporate such regulations in State Implementation Plans for oxidant control.

2. New Source Performance Standards. A comprehensive study of the synthetic organic chemical industry will result in federal standards to limit

new plant emissions of many organic compounds now uncontrolled. Guidance documents for control measures for existing plants also will be provided for use in State oxidant control plans.

3. Reactivity. The role of photochemical reactivity in oxidant control strategies will be re-examined with the assistance of State and local regulatory personnel, members of the technical community, and other concerned groups.

4. Substitutes for the Appendix J Model are being developed to provide a method for accounting for the effect of NO_x as well as oxidant and precursor transport. These new calculation techniques should provide more accurate quantification of the required reduction in organic emissions needed to achieve a desired oxidant concentration.

CONCLUSIONS

Recent technical findings indicate the need for oxidant control programs that span much broader geographical regions than orginally believed. Also, because of the role of transport of both oxidants and their precursors over time periods measured in days, even low reactive organics may have significant time to form oxidants and should be controlled. The EPA strategy, which emphasizes the control of anthropogenic organic emissions, is basically sound and programs are underway to establish more effective control of these emissions. The evolving oxidant control strategy places increasing emphasis on the control of emissions over broad geographical areas where emission densities are relatively high. States are being encouraged to apply reasonably available emission control measures in these areas as needed to supplement Federal standards for vehicle emissions and new stationary sources.

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PROBLEMS WITH CONVERTING STATE-OF-THE-ART PHOTOCHEMISTRY TO STATE LEVEL CONTROL STRATEGIES

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ABSTRACT

A brief history of the development of the photochemical oxidant control program in the State of Maryland is presented. Included in this history is a discussion of the effect of changes in Federal legislation, specifically, the 1967 Clean Air Act and 1970 Clean Air Act amendments on the photochemical oxidant control program.

In addition to this, the effects of changes in the state-of-the-art photochemistry are discussed in relation to the development of the photochemical oxidant control program in the State of Maryland. Specifically, attempts on the part of the State to develop an alternative to the Federally promulgated "Appendix J" are also discussed. Included in this is a discussion of the results of the use of aerometric data analysis and analytical simulation of smog chamber experiments.

Finally, observations on the effect of rapidly changing legislation and technology on the development of a state level photochemical oxidant control program are presented. In addition to this, recommendations for the development of a sound state level knowledge of photochemical oxidant state-of-the-art are outlined.

REVIEW OF THE PROGRAM DEVELOPMENT

Concern over automotive related air pollutants was first shown in the Maryland, Virginia, and District of Columbia region by the District of Columbia government as a result of a smog incident which occurred in June of 1959. An automobile nuisance abatement committee was formed and measurement of ambient levels of photochemical oxidants was initiated. Initially, these data were collected using the phenolphthalein grab gas method. When the Community Air Monitoring Program (CAMP) station was set up in 1962, the measurement technique was changed to the continuous, neutral buffered potassium iodide method. There were, however, no measurements made in the Maryland suburbs of the Washington, D. C. Metropolitan area. Ambient monitoring for oxidants began in Baltimore in 1964. The samples were usually taken during the middle of the day using the phenolphthalein 10 minute grab gas method.

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THE 1967 FEDERAL ACT

The accumulated photochemical oxidant data prior to the Clean Air Act of 1967 was compared to the existing California oxidant standard of 0.10 ppm to determine the severity of the Maryland problem. Although sparse, the data indicated that both Baltimore and Washington exceeded the standard less than twenty times per year and peak values were thought to be around 0.15 ppm. This problem when compared with that known to exist in California was given a second priority behind suspended particulates (TSP) and oxides of sulfur (SO_x).

According to the 1967 Federal Clean Air Act amendments, the issuance of criteria and control techniques documents by the Federal agency triggered the development of a regulatory program within state governments. In March of 1970, these documents were issued for photochemical oxidants and for oxides of nitrogen (NO_x). Following this event, the States were to establish ambient air quality standards protective of the public health and the appropriate control programs required to implement these standards. Throughout the summer of 1970, the available documents were reviewed and a preliminary assessment of control technology was assembled. The primary reference point was that of the compiled information contained in both the Federal criteria and control techniques documents; there had been no general awareness within the State of the problems or technological solutions associated with photochemical oxidants until 1970.

At the end of November in 1970 the State held public hearings at which the proposed ambient air quality standard to photochemical oxidants of 0.10 ppm was presented. The presentation report (1) also contained an assessment of the current levels and a preliminary finding of the necessary control program to implement these standards. As there were no modelling data shown in the criteria documents that would apply to ambient levels as low as those found in the Washington Region, the empirical diagrams showing the association between 6-9 a.m. non-methane hydrocarbons (NMHC) and afternoon oxidant peaks were used. One of these diagrams, found in the hydrocarbons criteria document (2), showed that peak oxidant values above 0.10 ppm were not observed when 6-9 a.m. NMHC levels were not above 0.30 ppm. Thus, a control program was sketched out that would reduce the mean levels of NMHC such that the peak value expected was less than 0.30 ppm NMHC. The available NMHC data showed this level was exceeded 97% of the time. Therefore, it was concluded that a major reduction in mean NMHC emissions was required in order to achieve the oxidant standard. The reduction of the mean 6-9 a.m. NMHC level from 0.65 ppm to 0.10 ppm equalled 85% control and was thought to be available through controls on solvent usage, gasoline marketing losses, dry cleaning vapor losses, and the adoption of the then proposed Federal new vehicle control program which provided a 90% reduction from precontrolled autos. The control strategy considered for solvent controls was based on California Rule 66, and was used simply because it was the only adopted regulation available at the time. The gasoline marketing controls were developed by the State as a system for reclaiming fuel vapors from the retail station filling process. The vapors were collected in the tank trucks and when the trucks returned to the gasoline terminals the processing took place. Terminal controls were patterned after those used in southern California and the controls were applied only to newly installed tanks.

In summary, the State thought that it had the beginning of a viable control program for obtaining the oxidant goal established pursuant to the 1967 version of the Federal Clean Air Act.

THE 1970 FEDERAL ACT AMENDMENTS

When the Federal Act was changed on the last day of 1970, the State postponed adoption of its ambient standard for photochemical oxidants until the Administrator of the newly created EPA could promulgate the national ambient air quality standards required by the amendments. During the year 1971, the majority of State effort centered around the development of new capabilities for measuring oxidants using a continuous, telemetered system of monitors of the chemiluminescence type. In addition, detailed inventories were compiled of all sources of hydrocarbons and extensive studies of mobile and stationary source technologies were begun. Land use and transportation studies were also begun. Throughout the summer and fall of 1971, regulations implementing the above controls were designed and presented at public hearings for both the Washington and Baltimore Metropolitan areas. The Implementation Plans which were required by EPA to demonstrate how the State intended to meet the photochemical oxidant standard were forwarded to EPA in December of 1971 and the regulations were adopted as law in March of 1972. In the process of generating the 1971 Implementation Plan for photochemical oxidants, the inventory of hydrocarbons was discovered to be less controllable than previously thought. This discovery was due to the facts found in the detailed technology review which showed more realistic reduction potentials than had been originally contemplated. The air quality forecasting model had changed, however, to a linear rollback of NMHC which was assumed to be proportional to peak oxidant. The change was based on the guideline included as Appendix J to the Federal regulations prescribing methods for preparation, adoption and submittal of implementation plans under the 1970 Act (3). In the range lower than 0.16 ppm oxidant, the guideline was so nearly linear that linearity was assumed. The rollback requirement for the Washington area changed from 85% based on hydrocarbons found in the preliminary survey to 50% based on the oxidant oriented Appendix J. Quite coincidentally, the revised estimate of the effectiveness of the planned hydrocarbon control program also showed a 50% emission reduction potential. The Baltimore oxidant measurements, however, based on the 10 minute grab phenolphthalein method prescribed a 30% reduction using Appendix J. Due to the greater industrial HC emission component in the inventory, the Federal new car program had a smaller impact on the Baltimore inventory. The proposed control program was predicted to net a 26% reduction in emissions which was considered sufficient for that time. Thus, the program designed under the 1967 version of the Federal Act was confirmed under the 1970 amendments. The State added Rule 66 type solvent controls and gasoline marketing controls to its arsenal of regulations. The drycleaning vapor losses were ignored as insignificant and also the drycleaning industry had been phasing out the use of photochemically reactive solvents. In addition, nitrogen oxides emissions were regulated but only for the sake of meeting NO_2 health standards, then thought to be exceeded. There was no consideration of NO_x emissions in the oxidant control program.

During 1972, the planning phase of the program started studies of the long term impact of alternative land use and transportation profiles. These studies were thought of as maintenance measures at that time. The overall program design parameters remained unchanged until the new continuous chemiluminescence system demonstrated peak ozone levels over 0.20 ppm. These new data plus the Natural Resources Defense Council vs. EPA court decision (4) forced development of an oxidant plan revision in mid-1973. This revision showed that a 70% reduction in 6-9 a.m. HC emissions was necessary to meet the oxidant standard, still using the Appendix J guideline. As a result, the State regenerated previously set aside plans for controlling drycleaning solvent losses and the emissions from gasoline marketing at existing stations. Regulations were adopted for this purpose in October, 1973. Two months later a regulation was added which was designed to prohibit new major HC sources and freeze the inventory of emissions from existing major sources in the Baltimore and Washington metropolitan areas. The most significant feature of the December, 1973 regulations from the ozone formulation standpoint, was the use of the term photochemically reactive organic material (PROM) in the regulation. For the first time the program directly considered reactivity in its oxidant control program, and such reactivity controls were based on reducing the production of ozone, not eye lacrimators, as was the case in California.

During the same period in the winter of 1972-1973, the State was considering the air quality impacts of the newly proposed Brandon Shores power plant to be located in the Baltimore metropolitan area. Since this plant was to be a large emitter of NO_x, the State wanted to determine the impact on photochemical oxidant levels within the region. Unfortunately, the Federally provided guideline was incapable of evaluating anything but the effect of NMHC on oxidant levels. As a result, the State launched an empirical exercise aimed at evaluating the aerometric data from the then operational continuous, telemetered system. The objective of this study was to develop a statistical relationship between oxides of nitrogen and ozone for the Baltimore-Washington metropolitan areas.

The first of two attempts at developing a suitable relationship used an eigenvector analysis which attempted to isolate the major determinants in the production of ozone. This analysis which was similar in concept to that of Peterson (5) used data from the six AIRMON stations for selected days during the summer of 1972. The ozone data for a given day was arranged in a 6 x 24 matrix (6 stations x 24 hours). From this matrix, it was possible to derive a set of empirical orthogonal functions which could then be analyzed for possible physical significance. The orthogonal functions consisted of two matrices. One matrix was 6 x 6 and the vectors in this matrix were related to station located parameters. The second matrix was 6 x 24 and consisted of vectors which were related to time of day.

This process was repeated for a number of days during the summer of 1972. The first orthogonal function, in most cases, accounted for 85-95% of the variance in the data. The first vector which was related to time of day correlated well with temperature or solar angle for the test day. Since the first orthogonal function accounted for most of the variance, no other significant features of the data could be isolated. Based upon these rather disappointing results, this technique was abandoned.

Since the first attempt resulted in no information of value relating to NO_x, a second analysis using multiple correlation was tried (6). The analysis technique was patterned after an exercise performed by Merz, et al. (7) on Los Angeles data.

The Maryland data used in this analysis was for May through August, 1972 and came from the six AIRMON stations located in the Baltimore-Washington metropolitan areas. Four of the stations were located in the Maryland suburbs of Washington approximately 8 miles from the central business district. The other two stations were located in Baltimore City. One station was approximately one mile from the central business district. The other station was approximately two miles from the central business district. Each of the stations measured the following parameters; nitric oxide (NO), nitrogen dioxide (NO_2), methane, total hydrocarbons and ozone. Due to instrument malfunction and non-valid data, the total amount of data available for this analysis was only 350 station-days. This amount of data was further reduced based on considerations of station location. Two stations were located near major roadways and the corresponding levels of oxides of nitrogen were significantly higher than for the other four stations. One of the remaining stations was located in a field, far removed from sources of oxides of nitrogen. This station was removed from the analysis due to the fact of significantly lower levels of oxides of nitrogen. Thus, three stations remained, two in the Washington suburbs and one in Baltimore City. The resulting number of station-days of data was 159. Meteorological data for the analysis came from the National Weather Service office at Baltimore-Washington International Airport.

Since none of the three stations had sufficient data to do a station specific analysis, all the available data was used and analyzed collectively. No consideration was given to atmospheric transport. The correlations, also, assumed that measured levels of precursors at a given station were related to maximum ozone values measured later in the day at the same station.

This analysis yielded the following results. The most significant variable in predicting ozone concentrations was temperature. The next most significant variable was the 6-9 a.m. average NO_2 concentration. The least significant variable was 6-9 a.m. average NMHC. The following equation summarizes the best correlation which this analysis of data produced.

$$\ln(\text{peak}(O_3)) = -16.772 + 0.23\ \ln(NO_2)_{6\text{-}9\text{ a.m.}} + 0.061\ \ln(\text{NMHC})_{6\text{-}9\text{ a.m.}} + 3.36\ \ln(\text{Max. temp.})$$

Where O_3, NO_2 and NMHC - concentration in ppm
Max. Temp. = Baltimore-Washington International Airport maximum temperature in degrees Fahrenheit.

The multiple correlation coefficient was 0.673 and the percent of the variance explained by this correlation was 45.1.

Based upon the correlation analysis, the Bureau concluded that NMHC control would have little or no effect on afternoon ozone levels. From this analysis it appeared that NO_x emission control would have a greater effect on afternoon ozone levels. However, it was recognized that the correlations did not explain a large portion of the variance and further correlations would be attempted as more data become available.

This work was forwarded to EPA's National Environmental Research Center (NERC) for review and comment with the intention that the relationship derived might be used in program planning work. The response was critical of the conclusions drawn from the study; that is, NERC did not believe that the study justified controlling NO_x instead of NMHC as a means for reducing ozone levels. Similar critical review by the California Air Resources Board found flaws in that the data base was limited, the State did not consider transport and other problems.

During the confusion that attended the preparation and submittal of Implementation Plans for the entire State, the photochemical aspects of hydrocarbon emissions were once again examined. Even though the mid-1973 submission was based on Appendix J, the State was interested in the relative degree of control afforded by taking reactivity into account. As a result, during the fall of 1973, the State prepared an inventory of HC emissions based on reactivity factors for ozone formation. These factors were being given preliminary consideration in mid-1972 by the atmospheric chemistry group in NERC and had been used by EPA in the demonstration project for transportation control strategy development for Los Angeles completed in December, 1972 (8). Following submission to the Philadelphia regional office of EPA, that agency chose not to use reactivity in its analysis and promulgated transportation control strategies based on the use of Appendix J and NMHC emissions. This action immediately followed the same action in Texas where the EPA promulgated a plan based on a reactive inventory and linear rollback.

In the beginning of 1974 the State challenged EPA over its promulgation in the fourth circuit court of appeals. Thus, while the judicial system was engaged to sort out the program design, the State continued to implement the non-controversial elements and initiated other studies on the photochemical phenomenon. Since the continuous, telemetered air monitoring system had produced a sizeable quantity of information on the subject, it seemed that more statistical analysis of aerometric data was in order. Thus, during the first half of 1974, the earlier multiple regression analysis was duplicated using the more extensive data. No significant change in the relationship of the parameters resulted.

In addition, a hypothesis was advanced that was intended to shed light on the EPA's hydrocarbon-only control guideline, Appendix J. The theory was advanced that if automotive traffic was significantly less prevalent on weekends than on weekdays, it should follow that significant reductions in ozone would also be observed. Such a study was carried out and the results reported in the literature (9). It was found that significantly lower levels of NMHC were measured on weekends with no commensurate reduction in ozone. Indeed, it was observed that weekend ozone levels may even be higher than the weekday measurements, however, the analysis did not demonstrate this point.

During the early summer of 1974, the State took an opportunity to analyze new aerometric data gathered at a rural site in Southern Maryland. Although a limited amount was available, wind directions were correlated with ozone and precursors along with corresponding data in Washington, Baltimore and the Tidewater, Virginia area. For the first time the State had first-hand experience with rural ozone levels and indications at that time were that transport of ozone was occurring from areas outside the State boundaries. This observation was qualitatively compared with work performed for EPA by the Research Triangle Institute which had measured ozone and precursor levels at McHenry, Maryland in the westernmost portion of the State (10).

Following the above work, a careful scrutiny of Appendix J revealed a flaw that had not been mentioned by others. Regardless of the lack of a cause-effect relationship, the so-called "observational" approach from which Appendix J was taken still showed that for given levels of hydrocarbons, many ozone levels were observed. Thus, the fundamental equation between the two variables was an inequality with an upper boundary observed. Thus, the fundamental equation between the two variables was an inequality with an upper boundary observed on the empirical diagram. This boundary, slightly modified, was transformed linearly by subtracting 0.24 from each hydrocarbon level and dividing the difference by that hydrocarbon level. Thus, the percent reduction necessary to achieve the Federal 6-9 a.m. NMHC guideline was given as a function of peak afternoon ozone measurements. The mathematical flaw is that an equality was presented as the Appendix J guideline where an inequality should have followed the transformation. Correctly presented, the label for the abscissae should have read Minimum Reduction in Hydrocarbon Emissions Required to Achieve National Standard for Photochemical Oxidant. Because of this error, the State of Maryland (and possibly a number of other States) were led to believe that a lesser degree of NMHC control was necessary in order to achieve the national standard for photochemical oxidants. Behind Appendix J, after this mistake was realized, the goal remained the same as that used during the first exercise in 1970, that is, the National guideline of 0.24 ppm 6-9 a.m. NMHC.

Program Revision Beginning in 1974

In mid-year 1974, the State decided that not enough effort was being devoted to understanding the basic state-of-the-art photochemistry of air pollution. As a result, a staff reorganization was ordered and two scientists were assigned to work full-time on the problem. The first task was to institute a very extensive literature survey of both theoretical and practical aspects of photochemistry literature with the overall objective to determine if the majority of observations were consistent among each other. Up until that time the results of State efforts seemed contradictory to the path of National policies.

One year later, the literature survey was essentially completed with a summary paper having been written. This paper was intended as an educational exercise for members of staff routinely dealing with hydrocarbon abatement activities. It also was to serve as a base which staff can update yearly to make sure that the State remains well aware of all latest studies.

It was discovered also that when taken in perspective the State was not yet ready for the analysis technique being highly touted by some, that is, the general photochemical oxidant simulation model. These models which incorporate both atmospheric diffusion processes and atmospheric photochemistry require more input data than the State can adequately provide at this time. Therefore, while these models provide a very useful learning exercise, the quantitative results of a detailed strategy analysis would be of uncertain accuracy. This opinion was based on both the paucity of reliable input data which the State could provide and the reported analysis of the performance of the models.

The most reasonable second generation planning model appeared to be the use of the smog chamber simulation data once demonstrations were available that were carried out over the full range of ambient precursor concentrations (11). In order that these chamber experiments could be fully utilized by the State, however, the agency personnel had to feel fully confident that State air quality would behave similarly. In February of 1976, therefore, the University of Maryland was engaged to provide a smog chamber simulator. The main objective is to provide the simulation tool such that State personnel can evaluate the reactivities and dynamics of Maryland-based emissions inventories and hopefully gain "hands-on" experience with photochemical reactions. It was also desired that the feasibility of the hybrid-analog computer be evaluated for these simulations since many linked equations appear in the set of chemical kinetics under study (12). The objective is to provide inexpensive simulation from short run times, rapid turnaround time and low cost facilities. Available digital programs will be utilized if the use of the hybrid does not perform adequately. In the meanwhile, the State has begun to collect a detailed emissions inventory to use for input. Emission questionnaires have been sent to approximately 80 stationary sources of organic emissions. These sources account for approximately 25% of the total anthropogenic emissions of organic compounds in the Baltimore metropolitan area. The information which the State is requesting includes operating schedules in terms of shifts per day, days per week, weeks per year and information on percent of yearly production by month. Emissions information is also being provided by the stationary sources in terms of composition of organic emissions. This information is in addition to the existing, non-species specific organic emission inventory. This data will provide a basis for future modelling efforts. Naturally, since this is the first attempt in the State at compiling such an inventory, problems are occurring. However, it is envisioned that this will be a continuing program and the quality and quantity of the information will improve as time progresses.

Observations

With the changes initiated by Congress in the 1970 Clean Air Act amendments and subsequently promulgated "guidelines", there began a series of rapidly fluctuating program design changes. The major changes were from a program design based on observations of non-methane hydrocarbons during the 6-9 a.m. period to an oxidant control strategy based on observed levels of ozone. With the newly discovered levels of ozone measured using EPA approved methodology, the program design changed once again. Much more restrictive program design requirements were expected since the 1970 amendments provided for an auto control program that was not phased in with the ambient air quality implementation deadlines contained in the Act. Program design persons were puzzled when long-term abatement needs disappeared. Within five years the hydrocarbon control requirements had made a complete cycle and those abatement needs are perhaps more restrictive now, than originally contemplated in 1970. Such a loop was the direct result of a mathematical error contained in the Federal Appendix J guideline used in evaluating State proposals and promulgating State Implementation Plans.

Throughout those areas of the Nation which were plagued by elevated ozone levels, there appeared to be different techniques utilized by the EPA in evaluating proposed plans and promulgating rules to abate such levels. California, Texas and Colorado were allowed to use an approach based on linear rollback of a reactive inventory while others, including Maryland, were not. No apparent reason for this is known to the State of Maryland. The use of such a reactive inventory in Maryland would have removed the requirements for those onerous strategies promulgated by the EPA that were largely the impetus for the State seeking relief from the Federal 4th circuit court of appeals.

From the extensive literature survey, it was found that almost all of the observations reported in the literature are consistent with one another. The conclusions of some papers, however, were found to have been drawn incorrectly due to a lack of overall perspective of the state-of-the-art. Such was the case with investigations made prior to the end of 1974 by the State of Maryland.

An emerging issue appears to be that of the occurrence of ozone levels far removed from urban areas. It seems that the extent of the ozone problem proportionally follows the expansion of the ambient air measurement system. Although there are schools of thought on the origin of those ozone levels, much controversy remains over whether second or third day reactions are responsible or the transport of "mature" ozone or even the reaction of surplus nitrogen oxides with rural emissions of both natural and man-made reactive hydrocarbon species.

CONCLUSIONS

Throughout the six year period that Maryland has been developing an oxidant abatement program, much confusion has attended the cause-effect relationships which result in observations of elevated levels of ambient ozone. Most of the confusion was resolved when it was realized that part-time efforts to understand the photochemistry of air pollution were not sufficient to understand the state-of-the-art. It is recommended that States with ozone problems fund and develop at least one full-time position for an expert in such matters. It is also recommended that the Regional offices of EPA do likewise.

In addition there appears to be an emerging phenomenon relating observed levels of ozone in rural areas to man's activities. There are several different theories behind the cause of the phenomenon although none of the hypotheses have been adequately tested. From the State level viewpoint, it is difficult to perceive if a uniform National policy exists and in particular, if the Congress has been advised to relax nitrogen oxide controls without regard for the rural problem. Is it possible that the same confusion which exists in the State ranks also pervades our national legislators? Hopefully, this is not the case.

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OXIDANT CONTROL UNDER SECTION 110 OF THE CLEAN AIR ACT

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ABSTRACT

Section 110 of the Clean Air Act requires states to submit plans that contain measures designed to attain and maintain the national standard for photochemical oxidant. The original State Implementation Plans were submitted in 1972 and have been subject to revision since that time. The approach to oxidant control of the Environmental Protection Agency as well as that of most States has been directed toward control of organic compound emissions. A recent review has shown that many State Implementation Plans are inadequate to attain and maintain the national standard. While it is difficult in many areas to attain and maintain the standard because of the limited control techniques available, efforts are continuing to reduce ambient concentrations of photochemical oxidant with a view toward eventual attainment of the national standard.

INTRODUCTION

Section 110 of the Clean Air Act (1) of 1970 required submittal of plans for the implementation of control measures to reduce emissions of specified air pollutants in order to attain National Ambient Air Quality Standards, which were to be established by the U. S. Environmental Protection Agency (EPA). The Act required attainment of the national primary, (meaning health-related), standards within three years of plan approval by EPA. However, in certain circumstances, i.e., where one or more emission sources were unable to comply with the requirements of the implementation plan because the necessary technology or other alternatives were not or would not be available within the three-year period, the Administrator could grant a two-year extension. In most cases the date established for attainment of the national primary standards was May 31, 1975.

In addition to State Implementation Plans (SIP) required by section 110, the Clean Air Act also required a broader control strategy to reduce organic emissions and oxidant air quality. The Federal program has primarily focused upon the control of new motor vehicle emissions and new stationary sources of organic compounds. Mobile sources are a major contributor to anthropogenic emissions of organic compounds and thus the U. S. Congress, in Title II--Emissions Standards for Moving Sources--of the Clean Air Act, mandated control

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of new mobile sources. Specifically, the Act required that by 1978 hydrocarbon emissions from light duty vehicles be reduced by 90 percent, based upon 1970 light-duty vehicle emission rates. Additionally, the Act authorizes the Administrator of EPA to prescribe standards applicable to emissions from any class of motor vehicles or motor vehicle engines which in his judgment causes or contributes to air pollution capable of endangering the public health or welfare. As a result, the Administrator has proposed or promulgated emission limitations for diesel engines, motorcycles, and aircraft engines. The Act also required EPA to consider new stationary sources of air pollution. Section 111 of the Act requires the Administrator to establish Federal standards of performance for new stationary sources. These standards of performance would apply regardless of ambient concentrations of the specified pollutant. While these programs are required under Sections of the Act other than Section 110, the emission reductions obtained due to these programs are an integral part to implementation plan development.

HISTORY OF PLAN DEVELOPMENT

On April 30, 1971, the Administrator promulgated in the Code of Federal Regulations National Ambient Air Quality Standards for six air pollutants. Included in this promulgation was the national primary standard for photochemical oxidant. This standard was established as a maximum one-hour ambient concentration of 160 $\mu g/m^3$ not to be exceeded more than once per year. Another of the National Ambient Air Quality Standards promulgated was a national standard for hydrocarbons. This standard, 160 $\mu g/m^3$ maximum three-hour concentration (6-9 a.m.) not to be exceeded more than once per year, was intended to be used only as a guide in devising implementation plans to achieve the oxidant standard. While implementation plans for oxidant were required, no implementation plans, ambient monitoring, or other actions were required as a result of the hydrocarbon standard.

The State initiated programs were included in the SIPs submitted to EPA in 1972. The plans submitted at that time included a variety of stationary source control measures. Regulations for controlling organic emissions from stationary sources have generally followed one of two patterns. The two basic patterns are the Appendix B to the Part 51 regulations (2) and the Los Angeles organic emission control regulations. EPA has recognized deficiencies in both of these approaches to stationary source control or organics and has undertaken a task to examine, industry by industry, the availability of controls.

When the implementation plans were submitted in 1972, EPA recognized that many were deficient in their ability to attain the national standard for photochemical oxidant. As a result, in 1973, several transportation control measures were promulgated as part of the SIPs to help correct this deficiency. Since that time a major concern to States in their development of State Implementation Plans has been organic emissions from mobile sources. Control of emissions from mobile and mobile-related sources has been a two-pronged attack. The first of these is designed to reduce organic emissions by the imposition of controls on the source. Among these measures are included:

- Inspection/maintenance programs,
- Medium and heavy-duty vehicle retrofit,
- Ship and barge controls, and
- Vapor controls for gasoline marketing.

The second part of the control program is designed to promote the efficient use of transportation sources. The following four measures are examples of these types of regulations:

- Transit improvements,
- Employer/employee incentives,
- Parking management/restrictions, and
- Traffic management/restrictions.

REVIEW OF EXISTING PLANS

The Environmental Protection Agency conducted a review, from late 1975 to early 1976, of State Implementation Plans to determine if they were substantially inadequate to attain and maintain the national standards. This review of recent ambient air quality data has shown that a number of Air Quality Control Regions (AQCR's) had not attained the national standard for photochemical oxidant by June 1975 and are not anticipated, even with full implementation of existing regulations, to attain that standard for several years hence. As a result of this review, in July 1976 EPA notified the appropriate State Governors and responsible air pollution control agencies of the need for revisions to the control strategy portion of their implementation plan. These notifications of the need for revision were issued for 61 individual Air Quality Control Regions and eight entire states without identification as to specific Air Quality Control Regions (Figure 1). In the case of photochemical oxidant, these notifications included at least one Air Quality Control Region in 30 states, which compares to the total of 55 states and territories required to submit plans under Section 110 of the Clean Air Act. These calls for State Implementation Plan revision do not, however, include those areas where the implementation plans have recently been revised or are currently being revised.

Revised plans must be submitted to EPA for review and approval by July 1977. These plans must include all measures necessary to provide for attainment of the standard, and where attainment of the standard cannot be demonstrated, the plan must include all achievable emission limitations. The term "achievable" as used by EPA is intended to require the imposition of reasonable "technology forcing" control measures, rather than simply requiring "off the shelf" technology. All other measures required to attain and maintain the National Ambient Air Quality Standard must be submitted by July 1978. These other measures are intended to include, but are not limited to, transportation and land use measures and programs designed to reduce organic com-

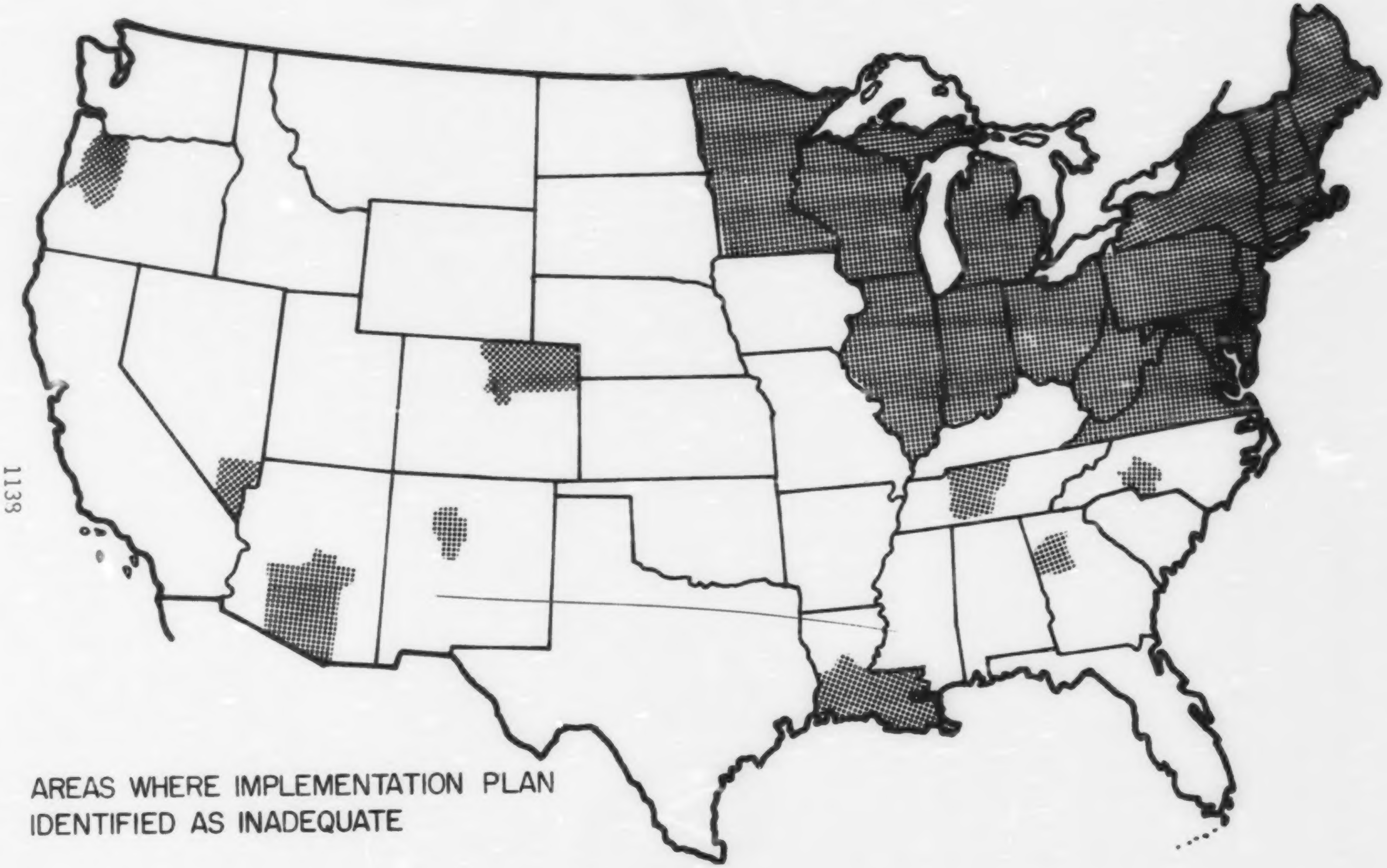

Figure 1. Areas where Implementation Plan identified as inadequate.

pound emissions. It is anticipated that some areas will be unable to demonstrate attainment of national standards. In such cases, the submitted plan should contain a discussion of the State's program to continue to identify and explore additional control measures and to adopt such measures when they are determined to be effective and workable.

IMPLEMENTATION PLAN DEVELOPMENT

During the first stages in the development of an implementation plan it must be determined which areas have ambient air quality levels that exceed the national standard of 160 $\mu g/m^3$. At the time of initial implementation plan development, it was felt that the photo-chemical oxidant problem was limited to major metropolitan areas. Since that time EPA and others have conducted several field studies and determined that ambient concentrations of photochemical oxidant greater than the standard may be observed even in rural areas of the country. While EPA recognizes the transport of photochemical oxidant (3, 4) and its precursors, it appears that the urban area emissions are the major contributor to ambient concentrations in excess of the standard in the vicinity of that urban area. One of the basic reasons for this is that a major portion of organic compounds emitted, motor vehicle exhaust and solvents, are highly reactive and form photochemical oxidant within a short period of time. As a consequence, EPA has generally recommended to the States that during the current implementation plan development process, control of emission sources in the urban area be emphasized.

The Clean Air Act dictates an air quality management approach. As a result, implementation plans must specify the reduction in emissions necessary to attain the National standard and how these reductions will be obtained. To assess the reductions necessary, a correlation between precursors to photochemical oxidant and maximum oxidant levels is required. The correlation generally used for the initial plan development in 1971-1972 was based upon the available non-methane hydrocarbon and oxidant air quality date (5) from a limited number of cities. This relationship, commonly referred to simply as Appendix "J" because it was published as Appendix "J" to the "Requirements for Preparation, Adoption, and Submittal of Implementation Plan," (6), has been severely criticized. Among the criticisms are the following points:

- The relationship is dominant at the upper bounds by data from Los Angeles, California,
- The relationship does not account for the effects of oxides of nitrogen,
- The relationship does not account for the effects of transport, and
- The effect of background levels of oxidant due to natural sources is not included.

In an effort to develop a more comprehensive relationship, the Environmental Protection Agency is continuing to study the correlation of maximum oxidant levels in relation to these and other factors. The EPA is currently attempting to develop several alternatives to the original correlation that can be used by State and local air pollution agencies to determine the necessary organic emission reductions to be used.

For many areas of the U. S. where the implementation plan has been identified as inadequate to attain the standard, these correlations indicate a requirement for organic emission control greater than is available with current control technology. As a result, many Air Quality Control Regions in the U.S. may not be able to demonstrate attainment of the national photochemical oxidant standard in the near future. Where this is the case, the submitted implementation plan must contain requirements to implement all reasonably achievable control technology for both mobile and stationary sources and must indicate areas where further investigation and study will be conducted to determine other mechanisms by which the oxidant standard may be attained. Further, EPA requires that State programs for control of mobile sources be coordinated with appropriate state and local planning and transportation agencies to ensure that air quality measures are implemented as part of the transportation planning process. In addition, the State will be required to adopt, as they become available and are needed, other regulations that are identified as representing reasonably achievable control technology. These procedures will likely require that the implementation plans submitted in 1977 and 1978 be revised in the future until the degree of control required to attain and maintain the national standard has been achieved.

EPA recognizes the important role of oxides of nitrogen in the photochemical process (3, 7, 8). However, recent studies have indicated that, except in certain circumstances, i.e., rural areas with low ambient levels of organics, the most efficient strategy for reducing ambient levels of photochemical oxidant is through reductions in organic compound emissions. In addition, EPA recognizes that as ambient levels of photochemical oxidant and organic compounds are reduced, it may be necessary in the future to consider the application of controls on sources of oxides of nitrogen emission (3). It is not anticipated that control of oxides of nitrogen, for the purpose of attaining the national standard for photochemical oxidant, will be required in the immediate future. Additional research is continuing in this area.

Natural sources of organic emissions are another problem which will have to be accounted for in the future. While natural sources of organic emissions may account for oxidant levels in the range of 0.04 to 0.05 ppm, it is believed that the contribution of natural sources is generally small in urban areas in relation to peak oxidant concentrations. Because EPA has recommended that implementation plans be developed for urban areas, the impact of natural sources is not a major concern in plan development at this time. However, various members of the scientific community and EPA are conducting research to determine the impact of natural sources of organics.

The Environmental Protection Agency recognizes the difficulties that will be faced as the U. S. progresses toward attainment of the national photochemical oxidant standard and remains committed to the basic goal of reducing ambient levels of photochemical oxidant. The long-range goal is to attain the national standard by reducing emissions of all organic compounds (except methane), since virtually all organic compounds eventually participate in the formation of photochemical oxidant when given sufficient time and ultraviolet energy. However, due to the fact that many areas of the country will not be able to attain the photochemical oxidant standard for several years, EPA currently requires that regulations requiring substitution of organic compounds classified as less reactive for those classified as highly reactive be included in the implementation plan. This measure will be used only as an interim measure until sufficient positive control measures for mobile and stationary sources are available to reduce emissions of organic compounds to a level so that the national standard will be attained. The regulations of this type currently in effect in many areas of the country are generally a modification of the Los Angeles Rule 66, which was based upon the hydrocarbon reactivity data available at the time of development. The EPA is currently assessing the need to (a) revise this regulation, or (b) develop an entirely new regulation based upon the most recent reactivity data available. It should also be noted that EPA is currently reassessing its policy on the use of reactivity and its requirement for adoption of substitution regulations. The Agency is also continuing to evaluate controls for existing sources and to develop standards of performance for new sources of organic compound emissions.

SUMMARY

EPA believes that the combination of motor vehicle controls, transportation control measures, definition and imposition of achievable control technology, regulations for substitution of organic compounds, development of standards of performance for new sources, and other programs will make up the total package of measures needed to attain and maintain the national photochemical oxidant standard. In addition, the U.S. Congress is currently considering amendment of the Clean Air Act to account for the need for consideration of differing types of control measures, the need to revise the Federal Motor Vehicle Control Program, and the need for additional time to implement control measures. The Congress is considering additional land use and transportation type measures for the control of all auto-related pollutant emissions and will likely require EPA to provide information on many new and innovative measures for control of mobile sources and to promote the most efficient use of transportation systems. While attainment of the national standard for photochemical oxidant in some areas of the U.S. may be difficult, continuing efforts by industry and local, State, and Federal air pollution control agencies will ensure that there will be continuing progress toward eventual attainment of the standard. Even though attainment of the national standard for photochemical oxidant may be several years away, EPA recognizes that there are many benefits, both to health and welfare, to be gained by reducing both maximum oxidant levels and the number of times the standard is exceeded.

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OXIDANT CONTROL STRATEGY: RECENT DEVELOPMENTS

B. Dimitriades*

ABSTRACT

Recent research findings relevant to atmospheric oxidant occurrence are reviewed and examined for implications regarding optimum strategy for oxidant control. Conclusions offered are that the recent evidence does invalidate the Appendix-J method for calculating control requirements but does not provide grounds for questioning the validity of hydrocarbon control as an approach to oxidant reduction.

INTRODUCTION

The first oxidant control strategy was put into effect in the U.S. in 1970. Experiences accumulated since then by the enforcement agencies have brought to surface some enforcement problems that were almost invariably blamed on the non-defensibility of this first control strategy. Furthermore, new research, conducted and reported in the last 3-4 years, raised additional questions on the validity of the current strategy and introduced numerous speculative -- but reasonable -- suggestions for revisions or for altogether new strategies. Because of the complexity of the problem of oxidant control and because of the confusing nature of some of the new research findings it was judged useful to review these latter findings and closely examine them for implications regarding optimum strategy for oxidant control.

CURRENT OXIDANT CONTROL STRATEGY

To help explain the relevance of and implications from the new research findings, the current oxidant control strategy will first be briefly described in terms of its key steps and assumptions.

The basic assumption underlying the current strategy concerns the physical and chemical mechanism of the overall process that starts with the discharge of emissions and terminates with the occurrence of oxidant at problem-concentrations. Thus, it has been assumed that emissions are discharged in the source areas and react in-situ to form oxidant that afflicts the "receptor" areas, the receptor areas being the very same source areas. Consistent with this assumption, aerometric data were gathered from several urban centers and were analyzed to derive a quantitative relationship between maximum-daily-oxidant concentrations and early-in-the-morning (6-9 a.m.) non-methane hydrocarbon (NMHC) concentrations; both the oxidant (O_x) and NMHC measurements were made in the same location, in the core areas of the urban centers. This relationship is known as the "upper limit" O_x-HC curve (Figure 1) (1).

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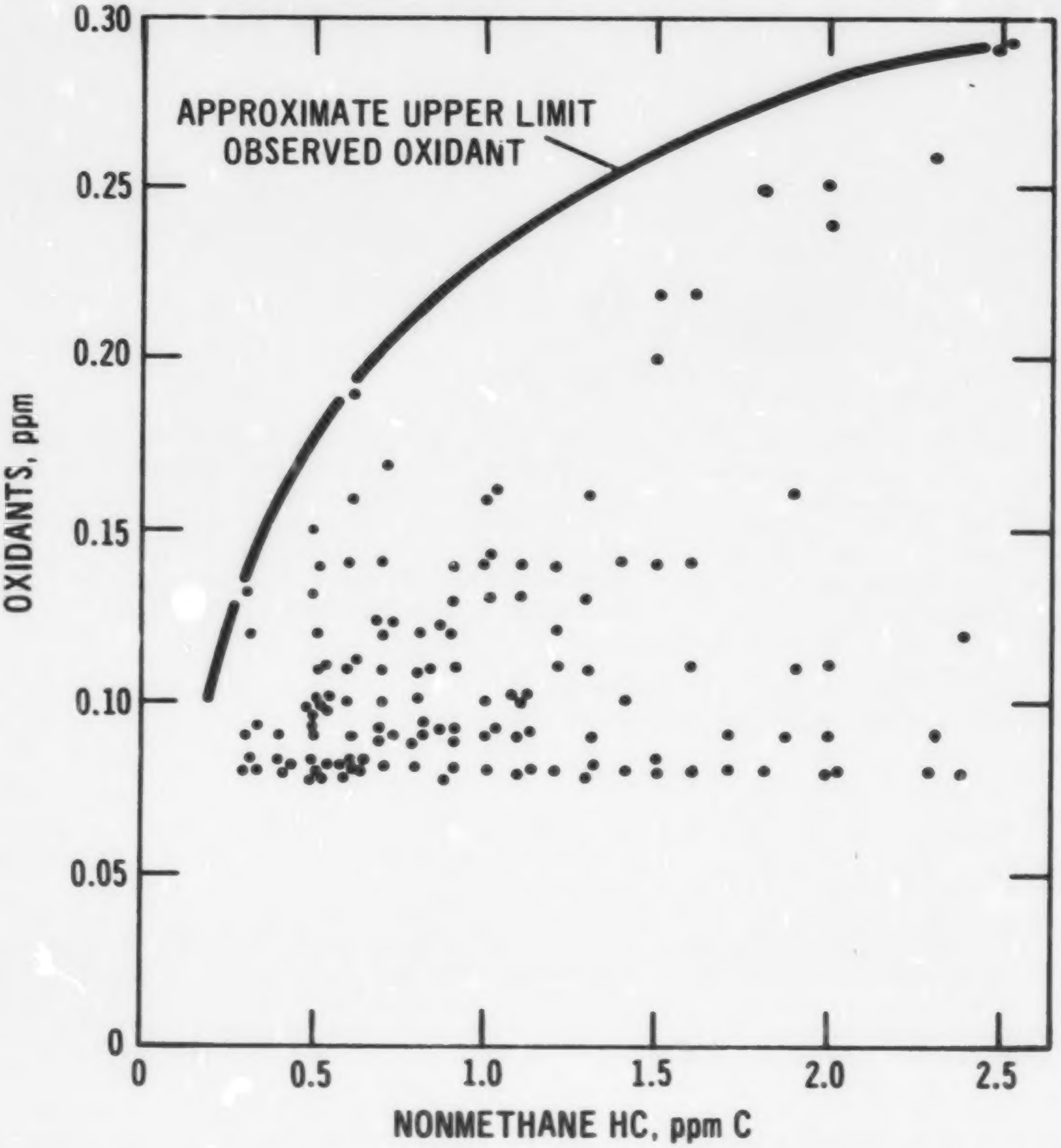

Figure 1. "Upper limit" curve relating ambient maximum 1-hour oxidant to 6-9 a.m. concentration of non-methane hydrocarbon.

Additional assumptions made were that all of observed O_x (and NMHC) arises from anthropogenic sources -- the natural background levels being zero -- and that ambient NMHC concentrations are proportional to NMHC emission rates. These assumptions and the "upper limit" curve were used to derive the Appendix-J curve relating ambient O_x air quality to NMHC emission control requirements (Figure 2).

A final key element in the current oxidant control strategy is that the emission control effort is focused on the urban centers. The non-urban areas are exempted from control but not totally; they are subject to the controls enforced in the form of national emission and new source performance standards.

The validity of this control strategy has been questioned both because of the questionable assumptions used and because of suspected ineffectiveness in reducing rural oxidant.

RECENT RESEARCH FINDINGS AND THEIR IMPLICATIONS

Briefly, recent research and findings can be summarized as follows:

1. Field studies have revealed the occurrence of a wide-spread O_x problem in rural areas (3).
2. Triggered by the findings on rural oxidant, extensive research has been initiated that has focused specifically on:
   - occurrence of short, mid-, and long range O_x transport (3-7)
   - meteorology related to O_x transport (6)
   - chemistry of photochemical oxidant formation under pollutant transport conditions (8)
   - role and importance of natural emissions as contributors to tropospheric oxidant (9)
   - stratospheric contribution to tropospheric oxidant (10, 11).
3. Smog chamber studies have resulted in an alternative (to Appendix J) method for calculating control requirements for urban O_x reduction (12, 13, 14). Key advantages of this latter method are the cause-effect nature of the chamber-derived O_x-to-precursor relationships, and the ability to consider the role of the NO_x factor quantitatively; the method, however, also has some serious limitations.
4. Smog chamber and field studies have indicated that the reactivity-related approach to control is less effective than previously thought (15, 16).

These findings, as well as the extent to which and the manner in which they can be used to support any immediate or future changes in the control strategy for O_x reduction, are discussed next.

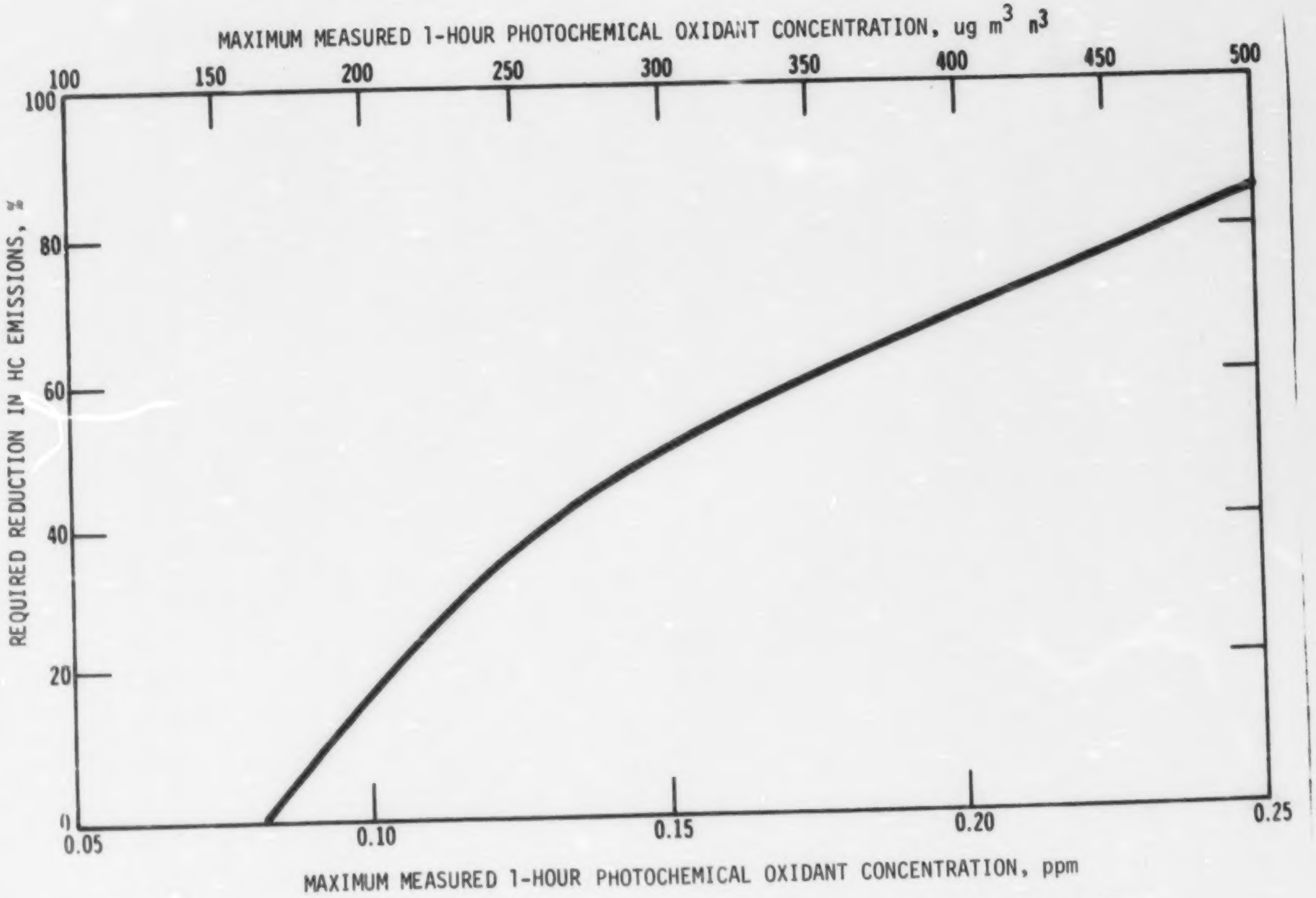

Figure 2. Appendix-J curve relating hydrocarbon control requirements with maximum measured oxidant concentration.

The occurrence of elevated (>0.08 ppm) oxidant levels in rural areas is a fact and need not be discussed further. What needs to be examined, however, is the relative magnitudes of the rural and urban oxidant problems in terms of effects and population exposure. Both the make-up of the rural oxidant mixture and the population exposed to rural oxidant are different relative to the urban case, and it could be that the rural problem is in effect less severe than suggested by the relative occurrence data. An appropriate assessment here certainly is relevant to the question of how adequate the current control strategy is, and therefore, needs to be made.

The studies on oxidant transport have shown conclusively that single-day, short-range transport does occur and may cause the oxidant problem to be more severe in the receptor areas (suburbs) than in the source areas (downtown) (3-7). The same studies have also provided indirect evidence that multi-day long-range transport occurs and impacts distant rural (and urban) areas downwind from the source areas. This latter evidence, however, is only qualitative, the degree to which transported pollutants account for the oxidant observed in the receptor rural (and urban) areas has not been established.

The control implications of the findings on short-range transport are relatively simple. These findings do not raise questions on the validity of the current strategy, except for the obvious deduction that unless such transport is considered the calculated degree of control needed will be too low. The relative roles of the HC and NO_x precursors under such short range transport conditions are not substantially different than those under no-transport conditions.

Unlike the short-range transport, the control implications of the findings on multi-day, long range transport are extremely complex. Thus, under long range transport conditions both the source-receptor relationship and the relative roles of the HC and NO_x precursors are different than those under no-transport conditions. The implication related to the source-receptor relationship factor is an obvious one. It simply means that in areas affected by transported oxidant, the Appendix-J curve is not valid because the source-receptor relationship is not the same as the one assumed in the derivation of the Appendix-J curve. The implications related to the oxidant-to-precursor dependency factor are not obvious and cannot be expressed simply in terms of an overall judgment. These latter implications merit a more detailed analysis presented next.

Present understanding regarding the relative roles of the HC and NO_x precursors is based almost entirely on smog chamber evidence and briefly is as follows. The difference in oxidant-to-precursor relationship between transport and no-transport systems arises from differences in irradiation time, and in extents of dilution and of interaction with fresh precursors. Thus, under long range transport conditions the HC-NO_x precursor mixture is irradiated, diluted and interacted by fresh emissions for several days, as compared to a few hours only for the no-transport systems. The combined effects of prolonged irradiation and dilution upon simulated emission-controlled and non-controlled atmospheres are illustrated by the data from a 3-day smog chamber test (Figure 3) (8). The pertinent observation to be made here

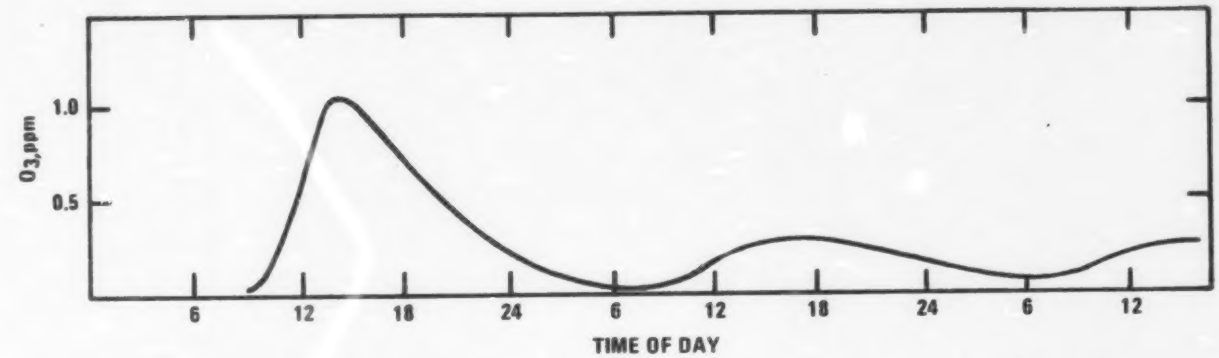

Figure 3. Ozone concentrations from three-day irradiation of HC-NO_x mixture. Mixture was diluted by 95 percent during first 24 hours.

is that in spite of reaction and dilution, the reacted pollutant mixture was capable of generating significant concentrations of O_x during the 2nd and 3rd days of irradiation. Obviously, the effect of dilution was to dilute resultant oxidant but less than proportionately.

The effect of hydrocarbon control is depicted in Figure 4 (17). It can be seen that control of hydrocarbons had a drastic effect upon the first day oxidant levels and a much lesser effect upon the second day oxidant levels.

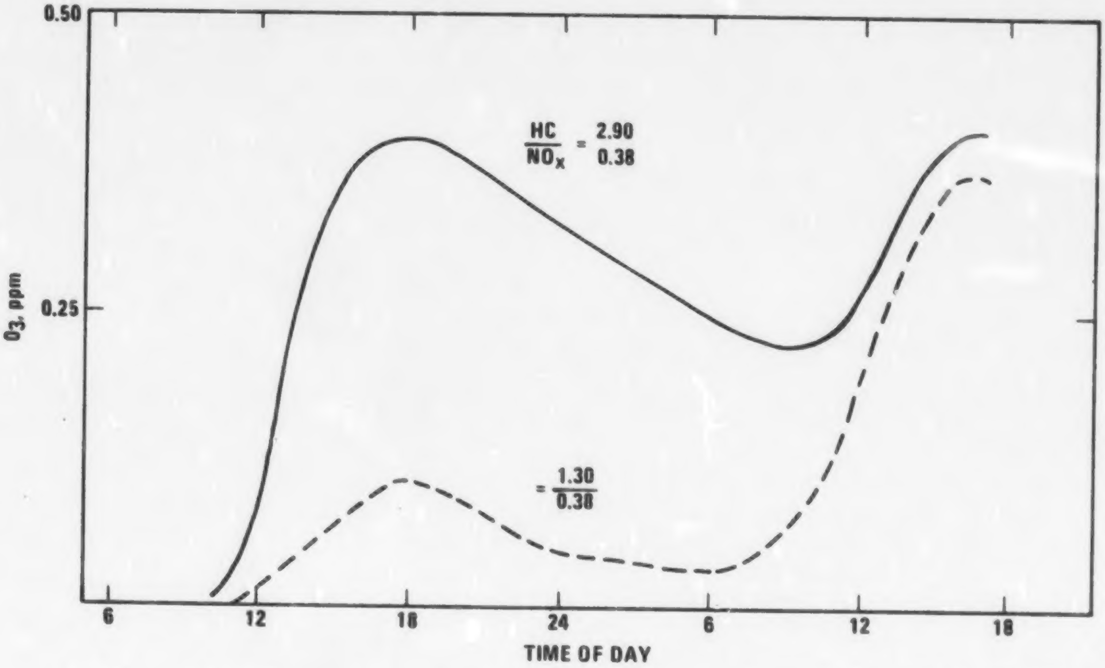

Figure 4. Second day O_3 formation from "non-controlled" and "controlled" HC-NO_x mixtures.

The effect of fresh precursor influx into the reacting system has not been determined; it can be speculated reasonably that it would be a complex function of the absolute as well as the relative levels of the reacted and fresh precursors.

The clear deduction from all these observations and expectations is that under long range pollutant transport conditions the quantitative relationships between oxidant and precorsors are indeed different than those assumed in the derivation of the Appendix-J method. Therefore, for areas affected by multi-day transported oxidant, Appendix-J is not the appropriate method for calculating numerical control requirements. Nevertheless, there is no indication that hydrocarbon control will not benefit such areas. What is somewhat in question is the effect of NO_x control upon such areas. This question is examined in some detail next.

Results from smog chamber experiments have shown that irradiation of an urban-like HC-NO mixture for one solar day results in a mixture which is virtually depleted of the reactive organics and has a much higher HC-to-NO_x ratio (8). Irradiation for a second day will further raise the ratio to as high as 100:1 or higher. At these high ratios, the reacted mixtures still retain their ability to form oxidant upon irradiation, even though the reactant HC is at only a few pphm and the NO_x at few ppb (8). Furthermore, injection of small amounts of NO_x seems to increase oxidant formation, suggesting that the role of NO_x in such "aged" systems, i.e., in urban air masses transported into downwind rural (or urban) areas, is contrary to the NO_x role in the atmosphere above the source area. These results may suggest at first glance that for reduction of rural oxidant it will be necessary to control NO_x along with HC. In actuality, however, such a conclusion may or may not be justified. The reasons for this uncertainity are as follows. Based on presently available evidence, control of NO_x will have two opposing effects:

(1) It will cause increased oxidant levels during the first day -- a part of the increment to be carried into the downwind rural (or urban) areas during subsequent days.

(2) It will result in an aged mixture containing less NO_x and, therefore, with less potential for oxidant formation in the downwind rural (or urban) areas.

The net result from these two effects is neither known or predictable, at present.

In conclusion, once again, the findings from recent research on oxidant transport, so far at least, have not provided grounds for invalidating HC control as the optimum approach to oxidant reduction in the source (urban) areas. Nevertheless, these findings do substantiate some of the criticisms against the quantitative bases of the current strategy (i.e., Appendix J), and raise some questions in regards to the effectiveness of the current strategy in reducing oxidant in rural areas. The next logical question is whether there are any options and what these options are, insofar as the rural oxidant reduction and replacement of the Appendix-J method are concerned. Replacement of the Appendix-J method is discussed elsewhere (13, 14). A brief discussion of the rural oxidant problem is given here, next.

Rural oxidant, conceivably, can arise from several sources, namely:

- From natural O_3 (from stratosphere and electrical discharge);
- From transported (urban) anthropogenic pollutants;
- From natural emissions acting alone or in mixture with anthropogenic ones;
- From local (anthropogenic) emissions acting alone or in mixture with transported ones.

Relevant evidence -- accepted or not -- reported lately on the relative importance of these sources is summarized as follows:

(1) Stratospheric O_3 can be transferred to the upper troposphere through a "tropopause folding" mechanism (10). However, the degree to which such O_3 reaches ground level has not been established. Based on radioactivity measurements, 24-hour-average estimates of ground level concentrations of stratospheric O_3 are well below the NAQS level (11). No estimates were possible, however, of the maximum 1-hour concentrations.

(2) Oxidant transport and its potential for rural oxidant buildup have been demonstrated repeatedly so that its occurrence is no longer in question. What is in question, however, is: (a) the importance of this rural oxidant source relative to the other sources, and (b) the dependence of such oxidant on the transported (presumably urban) HC and NO_x, and on the locally emitted (rural) fresh NO_x.

(3) Some natural hydrocarbons, namely terpenes, were found to be oxidant producers when mixed with NO_x at HC-to-NO_x ratios between 15:1 and 25:1 (9). Such low ratios do not occur in rural areas unless there are significant sources of anthropogenic emissions; in this latter case, terpenes could conceivably form oxidant. However, the importance of such oxidant in terms of concentration level, extent and frequency of occurrence is far from having been established. A similar function was proposed for methane also, with the suggestion that anthropogenic NO_x would be necessary for rural oxidant reduction (18). This latter evidence and conclusions, however, were rejected by others as erroneous (19, 20).

(4) Based on the recent understanding of transport phenomena, one could hypothesize reasonably that rural oxidant formation could be caused by local anthropogenic emissions in at least two meteorological situations:

   - Under conditions of severe stagnation, in which case the local emissions alone will enter the photochemical oxidant formation process. Such conditions may occur, e.g., within the center of a high pressure cell.

   - Within the back side of a high pressure cell, in which case the observed oxidant would reflect the sum total of urban and rural emissions dispersed within the high pressure cell. In such a case, obviously, the rural emissions will account for a fraction of the observed oxidant.

The statistics of severe stagnation cases coupled with elevated oxidant levels have been studied to some extent, and the connection between this stagnation factor and elevated oxidant concentrations has indeed been established (6). However, one would still have to consider that the severe stagnation conditions occur in a relatively small area only, within the high pressure cell. In the severe stagnation case, therefore, one cannot make a case for strong effects from rural anthropogenic emissions

In the back side of a high pressure cell, the rural and urban (anthropogenic) emissions should have relative effects roughly equal to their relative levels. Emission control, as prescribed by the current control strategy, will reduce mobile and stationary source emissions in the urban areas and mobile source emissions in the rural areas. Therefore, insofar as the rural problem is concerned, the current control strategy is inadequate only to the extent that it does not call for control of the stationary source emissions in the rural areas -- an inadequacy which cannot be serious.

From the preceding analysis of the rural oxidant problem and its connection to the current control strategy, it can be concluded that (a) at present, the rural oxidant problem is not sufficiently well understood, and, therefore, it is not possible to define the optimum approach to rural oxidant reduction, and (b) the current control strategy, while it may not represent the optimum approach, should nevertheless have a beneficial impact upon rural air quality.

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CONTROL REGULATIONS FOR STATIONARY SOURCES OF HYDROCARBONS IN THE UNITED STATES

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ABSTRACT

Stationary sources account for over 60 percent of the volatile organic compounds released to the atmosphere of the United States. While emissions from motor vehicles are being reduced, hydrocarbons from stationary sources are still increasing in many Air Quality Control Regions. Recently, the Environmental Protection Agency placed added emphasis on photochemical oxidants traceable to stationary sources and it is actively engaged in several programs aimed at reducing these hydrocarbon emissions.

Industrial sources of hydrocarbons can be grouped into three principal areas:

1. *The manufacture of organic chemicals,*
2. *The use of volatile solvents for such purposes as surface coating and metal cleaning, and*
3. *The transport, storage, and processing of crude oil and petroleum products.*

Major programs have been initiated in each of these areas to support establishment of new source performance standards and to review technology applicable to existing sources.

In assessing available technology, consideration has been given to process changes as well as add-on devices that recover or destroy organics present in exhaust gases. In view of the energy situation, the most acceptable approaches are those that effect reductions in use or recovery of hydrocarbon raw materials. The application of water-base paints in surface coating industries and vapor recovery in the gasoline marketing and dry cleaning industries are examples. Unfortunately, the most universally effective control technology--incineration--is also the most energy intensive, requiring natural gas or distillate oil as auxiliary fuel. The Environmental Protection Agency's approach has been to evaluate all of these options, including innovations in incineration technology, which can greatly reduce energy requirements. We envision that uniform or near uniform regulations could be applied to some

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industries, such as gasoline marketing. For surface coating and some types of organic chemical manufacture, uniform regulations may not be practicable. Here consideration may have to be given to specific aspects of the plant site and to product requirements.

Studies are underway to provide information on control technology to States and local jurisdictions and to support new source performance standards for metal degreasing operations, dry cleaning, various surface coating operations, bulk gasoline terminals, ship and barge transport of petroleum products, service stations, petroleum refineries, gasoline and crude oil storage and various other industries that utilize organic solvents or manufacture organic chemicals.

This paper presents a summary of the Environmental Protection Agency's current activities with regard to volatile organic control and will attempt to assess future trends in regulations.

CONTROL REGULATIONS FOR STATIONARY SOURCES OF HYDROCARBONS IN THE UNITED STATES

The strategy used to date to control photochemical oxidants has been the reduction of hydrocarbons and other volatile organic pollutants, with much of the effort directed at motor vehicles. Stationary sources haven't been ignored, but, except for the petroleum industry, few real reductions have been achieved in most industries. Nationwide, stationary sources remain at about the 1970 level and account for an estimated 62 percent of anthropogenic volatile organics. This result can be attributed both to growth and to the limited number of abatement strategies that have been employed to date.

Besides their oxidant potential, an ever increasing number of volatile organics cause concern because of proven or suspect toxic properties. In addition, we are faced with the suspicion that some halogenated organics are causing ozone depletion in the upper atmosphere. All this has caused the Environmental Protection Agency (EPA) to put increased emphasis on control technology for all types of volatile organic compounds and to further evaluate health effects of a tremendously large number of organics. Today I will review the types of volatile organic sources we are dealing with, how they can be characterized for control purposes, and the mechanisms that will be used to regulate their emissions.

Since 1970 nationwide emissions of man-made volatile organic air pollutants have declined only slightly from 34 million to 31 million tons annually, even though major reductions have been realized from motor vehicles. As can be seen in Figure 1, nationwide emissions have held steady at 19 to 20 million tons per year for stationary sources. While the pattern may be quite different in specific areas, on a national basis the growth of stationary sources is offsetting reductions effected by control measures. Additional reductions obviously are needed in many areas if this trend is to be altered.

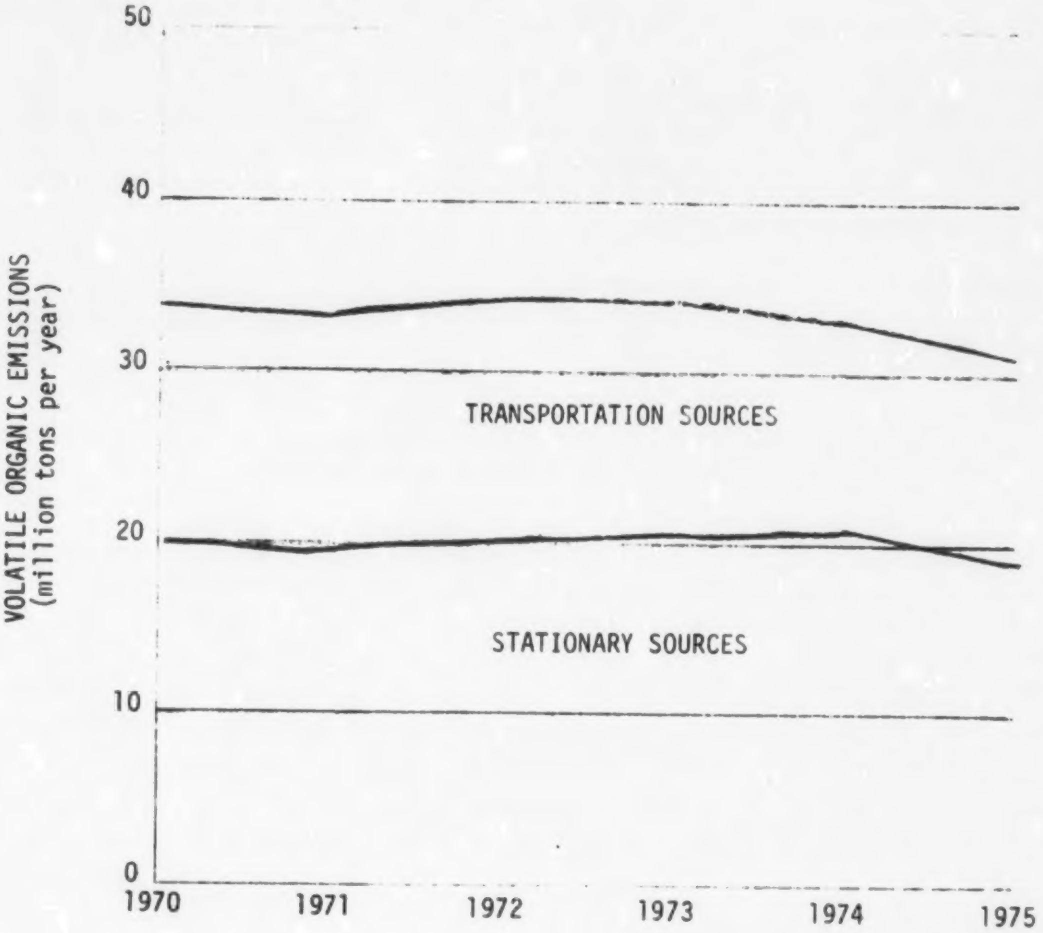

Figure 1. Trend in organic emissions - 1970 to 1975.

Let's look at the nationwide source inventory of Table 1 and consider where reductions would be most effective. Of the approximately 19 million tons per year attributed to stationary sources, small improvements can be expected in fuel combustion (1.4 TPY) and solid waste disposal (0.9 TPY), but it is doubtful if emissions (1.1 TPY) from forest burning and miscellaneous other burning operations will be significantly lessened. The greatest potential lies in industrial and commercial stationary sources that account for 82 percent of stationary source emissions and 52 percent of all anthropogenic organic sources in the United States. Industrial and commercial sources include the production, refining, and distribution of crude and refined petroleum products, the manufacture of chemicals and metals, and the so-called end-use solvent industries.

While control programs for these sources have been initiated in some parts of the nation--particularly California--and in a few cases have been fully acceptable, there often has been much disagreement over effectiveness, cost, and energy requirements of control technology. In some instances in the gasoline marketing industry, control devices not only prevent air pollution but also save product and money for the operator. Where control measures don't save enough product to offset control costs, acceptance has been slower. At the far end of the spectrum are measures that require removal of organic vapors from dilute exhaust streams, usually with no product recovery and at a measurable energy penalty.

While there are dissimilarities in exhaust gases from industrial and commercial sources, they usually can be categorized by the character and concentration of the organic(s), presence of other pollutants, and point(s) of emission. Major groupings are:

- Mixtures too rich to burn (10 to 40 volume percent hydrocarbon), such as those released from gasoline storage and transfer operations and some refinery and chemical processes.
- Lean mixtures (less than 0.5 volume percent hydrocarbon) often contaminated with particulate matter, such as those released from spray booths, baking and curing ovens, and many chemical manufacturing operations.
- Streams containing particulates, carbon monoxide, partially oxidized hydrocarbons, and/or sulfur compounds, such as those released from refinery catalyst regenerators, many chemical manufacturing processes, and a few metallurgical furnaces.
- Streams containing non-flammable halogenated compounds, such as those released from dry cleaning and degreasing operations.
- Dispersed, multi-point sources, such as pumps and valves in refineries and chemical plants.
- Waste disposal sites where solvents or other organics--often mixed with solids--are landfilled or otherwise discarded.

The applicability of add-on control options--incineration, condensation, absorption, and adsorption--is strongly influenced by stream characteristics. Exhaust streams containing rich hydrocarbon mixtures or halogenated solvents tend to be the most economical to control, often yielding a dividend through product recovery. For example, floating roofs on gasoline storage tanks (FRT's) usually pay for themselves in a short period. Vapor recovery at truck loading terminals is less cost effective than FRT's but recovered product can offset much or all of the control cost. However, several terminal operators have opted for less expensive incineration systems wherein displaced vapors are burned in flares with no product recovery.

The simple displacement or vapor balance system has been employed at gasoline service stations and bulk plants. It has also been used in unloading bulk solvents. The transferred liquid displaces a nearly equal volume of air/organic vapor to the dispensing vessel with any excess vapor venting to the atmosphere. Where vapor tight connections can be used, the system is efficient and highly cost effective.

Carbon adsorption can be used advantageously with halogenated solvents because of the value of recovered product as well as the non-flammable character of the solvent. Carbon finds frequent use in recovering chlorinated solvents in the dry cleaning industry and to some extent in degreasing. However, adsorption is seldom used with petroleum solvents.

The most costly exhaust gases to control are dilute streams where the hydrocarbon level is too low to sustain combustion, has little recovery value, and is frequently contaminated with sticky particulate. For these lean streams, incineration at 1200 to 1500°F is usually effective for air pollution control purposes but requires appreciable energy input in the form of natural gas or distillate fuel oil. Condensation and absorption are ineffective because hydrocarbon levels are too dilute. Adsorption can provide high removal efficiency but requires that particulates be removed beforehand to avoid contamination of the adsorbent.

In some industries--particularly surface coating--the most promising means of curtailing organic emissions are process changes that back out much of the input solvent or sharply reduce the volume of exhaust gases. Water-borne, high solids and powder coatings have all been employed to a limited degree in the manufacture of consumer goods. Where they are used, organic emissions have been lowered by 85 to 100 percent. Unfortunately, these represent well under 10 percent of the industrial surface coatings in use today. Acceptance of low solvent paints by the coating industry and its customers has been far less than was predicted a few years ago. Manufacturers' reluctance to commit to untested coatings isn't surprising since the products often are subject to severe conditions. Applications range from food and beverage containers to structural and mechanical products subject to marine atmosphere.

Architectural coatings are one area where low solvent content coatings have been highly successful. Today, water-borne paints account for about 70 percent of interior and exterior applications. While these coatings still contain about 20 percent organic solvent, they represent reductions of 75 to 90 percent over conventional oil-base paints.

In light of the diverse control possibilities for stationary hydrocarbon sources, EPA recently directed additional resources to the review and documentation of applicable technology. The aim is to publish control technology guidelines for principal sources and where applicable to promulgate new source performance standards and/or national emission standards for hazardous pollutants. At present, the bulk of this effort is directed at the control of oxidant forming non-methane hydrocarbons. At the same time, we are looking at the toxic effects of organic emissions, particularly those associated with chemical manufacturing processes. If and when it becomes necessary to apply more stringent controls to specific toxic materials or to organic halogens that impact the upper atmosphere, we should be in possession of sufficient knowledge to proceed with an effective control program.

With regard to toxic organic emissions, our greatest concerns are the chronic toxicants associated with carcinogenesis, mutagenesis, and teratogenesis. A compilation of available data is nearing completion by the MITRE Corporation that identifies over 600 organic compounds that are produced in large enough quantity, are volatile enough, and exhibit known or potential toxicity characteristics sufficient to warrant further study.

For oxidant control purposes, the program is aimed at reducing emissions of all volatile organic pollutants regardless of their photochemical reactivity. This course of action is based on review of smog chamber studies and appraisal of commercial solvents. These studies show very few organic compounds to be of "low reactivity"; furthermore, most of the latter are unacceptable as commercial solvents. Thus, solvent substitution strategies based on photochemical reactivity appear questionable at best. Nonetheless, this subject is being further reviewed to determine whether, in fact, some low reactivity solvents can be employed and whether solvent substitution would suffice as an oxidant control strategy for isolated areas of the nation where transport phenomena do not adversely affect downwind receptors.

EPA is assembling control technology information for a variety of petroleum-related industries, chemical manufacturing processes, and end-use solvent industries, as listed in Table 2. In some instances, a good deal of information has already been assembled. Briefly, developments and expectations are as follows:

- Gasoline Storage Tanks - The floating roof continues to be the dominant control device for large tankage, but EPA is making a renewed effort to evaluate vapor recovery systems. Most of the effort by EPA and the industry is directed at more positive measurement techniques for emissions from floating roof tanks. The current program should result in more definitive specifications for vapor seals and other components of floating roofs that affect emissions.

- Bulk Gasoline Terminals - Comprehensive tests are being conducted to more fully evaluate the effectiveness of vapor recovery systems, particularly in areas where service station controls are in effect. These data will be compared with the already completed evaluation of incineration devices. Test procedures are being standardized and the feasibility of various monitoring devices analyzed.

- Bulk Gasoline Plants - Contract studies will soon be completed to evaluate the feasibility of both vapor balance and secondary recovery systems at bulk plants. Of particular importance is the economic impact of control regulations on small operators. Large bulk plants are expected to utilize the same types of vapor recovery and incineration equipment that are being used at bulk terminals.

- Service Stations - Control systems for underground storage tanks (Stage I) have been installed in 1976 in many areas of the nation. For the most part, they are simple displacement systems that appear to provide well over 90 percent vapor recovery when operated properly. The effectiveness of existing systems and operating practices will be evaluated to determine if hardware improvements and/or operating restrictions are required.

The vehicle refueling (Stage II) program has proceeded much more slowly and there is still much uncertainty as to the effectiveness of the competing vapor balance and vacuum assist systems. EPA will repropose Stage II regulations this month and will continue to evaluate systems installed or being installed in California and a few other areas of the nation. Under the revised Stage II regulation, the first EPA mandated control systems would be installed in 1978.

- Ships and Barges - Most of the effort to date has been directed at the loading of gasoline into tankers in Gulf Coast ports. In addition, there is a great deal of interest in crude unloading both on the Gulf Coast and the Pacific Coast. Studies conducted by EPA and the petroleum industry indicate that emissions are not as great as originally predicted because the ullage space in the cargo tanks is well below saturation levels. Nonetheless, operating practices can greatly influence saturation and the magnitude of emissions during loading, ballasting of tanks, and during inerting and certain maintenance operations.

- Crude Petroleum Production - Studies of offshore drilling operations were recently contracted. Initial efforts will characterize emissions and review the more obvious control technology for storage, transfer, valves, pumps, and separators. A large fraction of emissions from production operations are believed to be methane, but heavier fractions are also released. In at least some instances, air pollution control equipment will recover substantial quantities of LPG feedstocks.

- Petroleum Refining - We plan to complete a guidelines document in mid-1977 covering blowdown systems, cooling towers, flares, valves, pumps, and other miscellaneous sources. Processing units are being evaluated under a major research and development contract. It is anticipated that equipment specifications and operating practices will be a large part of any process unit regulations. For those processes with discrete exhaust streams, emission limits can be expected.

- Chemical Manufacturing - Carbon black and a few other chemical processes have been evaluated, but EPA's major contract in this field will be a comprehensive study to be awarded within the next few months. Control measures in this area are expected to be extremely source specific. We are looking to incineration, adsorption, and absorption techniques as well as innovative process changes that can reduce the need for pollution control. Manufacture of the nine chemicals listed in Table 2 are important because of their toxicity as well as their impact on photochemical oxidants.

- Surface Coating - Principal contract studies in this area are nearing completion. We expect the eventual answer to solvent control to be a combination of improved coating materials and better application methods. Incineration and possibly adsorption are expected to supplement control programs, with incinerator designs to be maximixed for purposes of heat recovery and energy economy.

- Degreasing - Improvements in design and operation are needed to minimize losses and improve capture efficiency at the degreaser. We also expect that significant improvements will be achieved through better operating practices. Adsorption will continue to be the dominant stack gas clean-up technique.

- Dry Cleaning - Carbon adsorption is expected to become standard practice for most perchloroethylene plants. Even without control regulations, plants using fluorinated solvents will continue to maximize vapor recovery because of the cost of the solvent. The future of petroleum solvent dry cleaning is uncertain because of related problems of safety, economics, and energy requirements of available control technologies.

For all of these sources, consideration will be given to the promulgation of new source performance standards (NSPS) under Section 111 of the Clean Air Act or national emission standards for hazardous pollutants under Section 112. New source standards are the more likely vehicle. Hazardous pollutant standards are specific to the pollutant and apply to both new and existing installations. If the Section 112 route is chosen, emission limits will be established for all significant sources of the pollutant. To date, hazardous pollutant standards have been proposed for only one organic pollutant, vinyl chloride. The final regulations are expected to be promulgated shortly.

Where we are dealing with large identifiable sources of oxidant-forming organics, NSPS will be the choice. Thus, bulk gasoline terminals, refinery process units, major surface coating operations, and many chemical manufacturing operations are principal candidates for NSPS. In these instances, control technology, costs, and economic and environmental impact will be documented and the information made available to interested parties.

To cover existing sources, we intend to publish what we term "guidelines documents". The purpose of the guidelines is to apprise State and local jurisdictions of the effectiveness and costs of available control options. The documents will recommend no specific emission limits but will leave the choice of control level to the States. We anticipate that this approach will lead to source specific hydrocarbon regulations for many different industries. The greatest specificity probably will be applied to the chemical manufacturing and surface coating industries where both economics and feasibility can vary with the product and the service to which the product is subjected. Conversely, such industries as gasoline marketing, dry cleaning, and degreasing are well standardized; here we look for relatively uniform regulations, although degrees of stringency are expected depending on the desired hydrocarbon reduction needed in the particular area.

The first guidelines document was prepared for five surface coating industries--can manufacturing, fabric coating, paper coating, coil coating, and automobile assembly plants. A draft document was distributed in July to control agencies, affected industries, and other interested parties. The finalized document is scheduled for release in November. It will reflect the large number of comments we have received on the draft document.

In summary, to combat the oxidant problem and a growing toxic organic chemical problem, EPA plans to enact a number of new source performance standards and a few hazardous pollutant standards for sources of organic pollutants. State regulations will require increased control of organic emissions from existing stationary sources. All of these are likely to be in the form of positive reductions rather than substitution of less reactive solvents. Source specific guideline documents will provide information needed by the States to make decisions on emission limits, costs, and economic and environmental impact.

It is clear that a nationwide cleanup of organics is beginning and that it will have a major impact on almost all industries that use, handle, or produce organic materials.

TABLE 1. ANTHROPOGENIC SOURCES OF ORGANIC AIR POLLUTION IN THE UNITED STATES, 1975

	Emissions, 10^6 tons/yr	Fraction of Total Emissions, %
Transportation	11.7	37.6
Fuel Combustion	1.4	4.5
Forest, Agricultural and Other Open Burning	1.1	3.5
Solid Waste Disposal	0.9	2.9
Petroleum Refining	0.9	2.9
Oil and Gas Production and Marketing	4.2	13.5
Chemical Manufacturing	1.6	5.1
Metals Manufacturing	0.2	0.6
Other Manufacturing	0.8	2.6
Organic Solvent Usage	8.3	26.7
	31.1	99.9

TABLE 1A. CHARACTERISTICS OF INDUSTRIAL EXHAUST STREAMS CONTAINING VOLATILE ORGANIC POLLUTANTS

- Mixtures too rich to burn - gasoline storage and transfer, petroleum and chemical processes.
- Mixtures too lean to burn - surface coating, baking and curing ovens, plastics and rubber product manufacture.
- Streams containing particulates, CO, HC, SO_x, H_2S and partially oxidized organics - refinery, chemical and metallurgical processes.
- Streams containing halogenated organics - dry cleaning and degreasing.
- Multipoint Sources - pumps, valves, blowdown system, cooling towers in refineries and chemical plants.
- Waste disposal sites for solvents, chemical and petroleum plant wastes.

TABLE 2. SOURCES OF ORGANIC AIR POLLUTANTS BEING EVALUATED

PETROLEUM RELATED

STORAGE TANKS
BULK TERMINALS
BULK PLANTS
SERVICE STATIONS
  VEHICLE FUELING
  AND STORAGE TANKS
SHIP AND BARGE TRANSFER
PETROLEUM PRODUCTION
PETROLEUM REFINING
  PROCESSING EQUIPMENT
  FUGITIVE EMISSIONS FROM
  PUMPS, VALVES, ETC.

SOLVENT USE

SURFACE COATING
DRY CLEANING
DEGREASING
RUBBER PRODUCT MFG.
PHARMACEUTICAL MFG.
ADHESIVE MFG.
WOOD PRODUCT MFG.
PAINT MFG.

CHEMICAL MANUFACTURING

BENZENE
ACRYLONITRILE
CARBON TETRACHLORIDE
FORMALDEHYDE
MALEIC ANHYDRIDE
NITROBENZENE
PERCHLOROETHYLENE
TRICHLOROETHYLENE
VINYLIDENE CHLORIDE

ADDENDUM

Prepared Comments on Japanese Photochemical Air Quality Standards and Control Strategies, by Professor Raisaku Kiyoura, Tokyo Institute of Technology.

Following are some comments of mine and questions on the subject standards. In the opinion of several biologists concerning the relative toxicities of oxidants and NO_2, the adverse effects of oxidants are 10 to 20 times greater than those of NO_2. Therefore, control of oxidants is essential in air pollution control strategies. Until now, NO_2 has not been controlled as stringently as the hydrocarbon precursor of photochemical oxidants. However, some people believe that NO_2 may also have to be stringently controlled to achieve the air quality standard for oxidant.

The oxidant standards in Japan and U.S. have been set at the same level: 0.08 ppm (1 hour)*. The U.S. NO_2 standard was set at 0.05 ppm for annual average (equivalent to a 24-hour average of 0.14 ppm), and some biologists feel that one-hour-maximum standard for NO_2 is also necessary. The Japanese NO_2 standard of 0.02 ppm for 24-hour average is five to seven times stricter than that of the U.S., but there is some uncertainty whether this difference is justified by biomedical evidence.

Very stringent control of NO_2 without similarly stringent control of non-methane hydrocarbons could result in increased oxidant formation. Therefore, these pollutant emission levels must be kept in balance consistent both with the biomedical justification of the NO_2 and oxidant standards and with the relative roles of the NO_x and hydrocarbon precursors in the photochemical oxidant formation process.

Next, I submit that the following four questions need to be answered with respect to the air pollution situation in Japan:

1. Under such a low Japanese NO_2 standard, can Japan reduce oxidant formation by controlling HC?

2. If so, what is the ambient HC level in ppm that would need to be achieved?

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*The Japanese standard for oxidant was originally set at 0.06 ppm but was subsequently changed to 0.08 ppm for reasons related to the analytical measurement method.

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3. What is the relationship between the HC level and the natural background level?

4. Is that HC level attainable?

A guide level limiting nonmethane HC between 0.20 and 0.31 ppmC (from 6 to 9 a.m.) was recommended in August 1976 by an expert committee of the Japanese Central Council for Control of Environmental Pollution.